PB-214 902

RENOVATION OF WASTE WATER BY FOAM AND EMULSION FRACTIONATION

I. A. Eldib, et al

Esso Research and Engineering Company
Linden, New Jersey

1963

DISTRIBUTED BY:

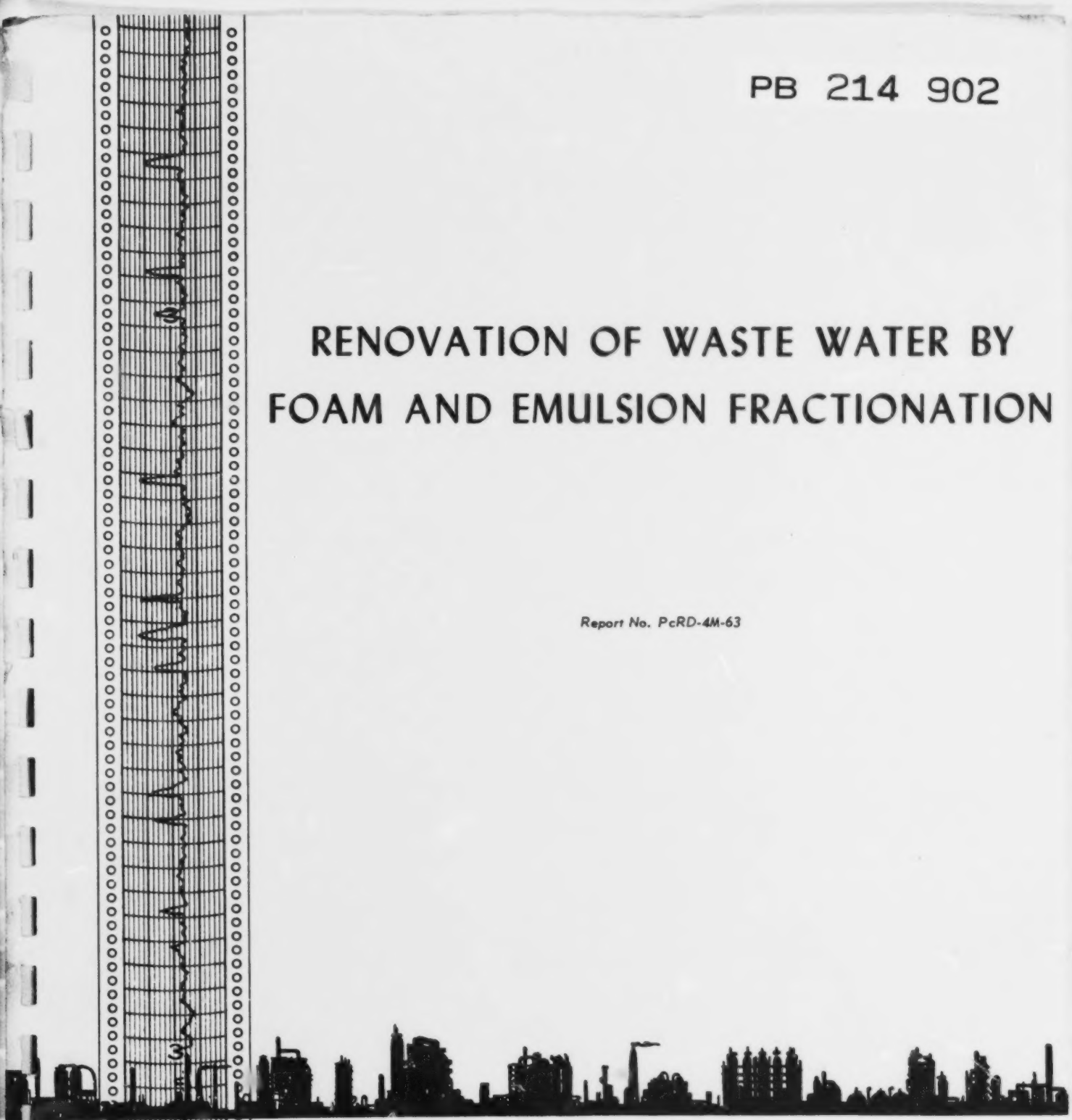
NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 214 902

RENOVATION OF WASTE WATER BY FOAM AND EMULSION FRACTIONATION

Report No. PcRD-4M-63



PROCESS RESEARCH DIVISION
Esso Research and Engineering Company

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

147

RENOVATION OF WASTE WATER BY FOAM AND EMULSION FRACTIONATION

I. A. ELDIB
R. M. SKOMOROSKI

WORK DONE UNDER CONTRACT NO. PH 86-62-26 FROM U.S. PUBLIC HEALTH SERVICE TO ESSO RESEARCH AND ENGINEERING COMPANY.

PROCESS RESEARCH DIVISION
Esso Research and Engineering Company

PcRD-4M-63

TABLE OF CONTENTS

		Page
I.	SUMMARY	1
II.	INTRODUCTION	3
	• Foam Fractionation Investigated For Removal Of Soluble Organics From Waste Water	3
	• Foam Fractionation Studied In Combination With Adsorption	4
	• Emulsion Fractionation Investigated For Removal Of Soluble Organics	4
	• Scope Of The Work	4
III.	SOURCE OF WASTE WATER EFFLUENTS	7
	• Bergen County Sewage Authority Waste Treatment Plant	7
	• Waste Water Treatment Plant In Bernardsville, N. J.	8
	• Middlesex County Sewage Authority Waste Treatment Plant	8
	• Problems Connected With Variation Of Waste Water	8
IV.	ANALYTICAL PROCEDURE	11
	• Waste Water Effluents Filtered Before Foaming	11
V.	FOAM FRACTIONATION STUDIES	13
	A. Equipment And Procedure	13
	• Batch Equipment And Procedure	13
	• Continuous Equipment And Procedure	14
	• Criteria Used To Interpret Results	14
	B. Batch And Foam Fractionation	19
	• Both Primary And Secondary Effluents Were Foamed	19
	• Foam Fractionation Effectiveness Depends To Some Extent On Gas Bubble Size And Column Diameter	19

TABLE OF CONTENTS (CONT'D.)

	Page
• Foam Fractionation Removes Soluble Organics Other Than ABS	21
• A Major Part Of ABS Is Removed In Initial Fraction Of Foam Overhead	21
• Temperature Effect Appears To Be Small Over 35-75°F. Range	23
• Short Residence Times Are Sufficient To Remove Most Of The ABS	24
• Variation Of pH Studied To Improve Removal By Foam Fractionation	24
• Effect Of pH On Foam Of Secondary Effluent	25
• Best Data, Show Enrichment Of ABS And COD In Foam Improved At pH Higher And Lower Than 7	25
• Scheme Of Foaming, Altering pH, Then Refoaming Does Not Improve Removal Of ABS Or COD	26
• Additives In Low Concentrations May Improve COD Removal	27
• Good Foam Drainage Reduces Volume Of Foam Rejected	28
• Refoaming To Reduce Foam Reject Cannot Be Carried Out Many Times	29
• Refluxing Foam Overhead For Short Times May Increase COD Removal	31
• Effect Of Different Gases On Removal By Foaming	32
VI. FOAMING DISTILLED WATER CONTAINING VARIOUS SURFACTANTS	33
• Effect Of pH On Foaming Solutions Of Synthetic Detergents	33
• Foaming Solutions Containing Low Concentrations Of ABS	34
• pH Affects The Surface Tension Of Proteins And Detergents	34

TABLE OF CONTENTS (CONT'D.)

		Page
	• Ion Pairs Offer Lead To Removal Of Weak Surfactants	35
	• Proteins And Detergents Interact And Form More Foam Than Either One Alone Does	36
	• Interaction Between Detergents And Protein Improve Separation By Foaming	36
VII.	CONTINUOUS FOAM FRACTIONATION	39
	• Continuous Foam Fractionation Experiments	39
	• Certain Minimum Gas Rates And Residence Times Are Required For ABS Or COD Removal	39
	• Ratio Of Volume Of Gas/Volume Of Liquid Provides General Correlation For Continuous Data	41
	• Analysis Of The Foam Fractionation Operation As A Dynamic System	42
	• Model I	43
	• Assumptions	44
	• Material Balance	45
	• Model II	49
	• Assumptions	49
	• Material Balance	49
	• How Does Mathematical Model Of Foaming Operation Help In Practical Situations	54
VIII.	FOAMING IN COMBINATION WITH ADSORPTION	57
	• Adsorption Preceded By Foaming Can Give Low COD	57
IX.	EMULSION FRACTIONATION	59
	• Emulsion Stability Of Secondary Effluent With Organic Solvents Determined	59
	• So Far Emulsion Fractionation Does Not Look Promising For Removal Of Soluble Organics	59

TABLE OF CONTENTS (CONT'D.)

		Page
X.	ECONOMICS OF FOAM FRACTIONATION PROCESS	61
	• Case Studied	61
	• Process Basis Specifications	61
	• Equipment Design	61
	• Capital Costs	63
	• Operating Costs	63
	• Cost Of Altering Waste Water pH Is Moderate	63
XI.	RECOMMENDATIONS FOR FUTURE WORK	67
XII.	PATENTABLE FEATURES	69
XIII.	APPENDICES	71

I. SUMMARY

A study was made to evaluate the feasibility of using foam fractionation alone, or in combination with carbon adsorption, to remove detergents and other water soluble organic impurities from waste water. Emulsion fractionation was also evaluated briefly as a waste water purification technique. Future population growth in the U.S. is expected to require more fresh water than is presently available and the Esso Research and Engineering Co., under contract No. PH-86-62-26 from the U.S. Public Health Service, has studied the feasibility of using foam fractionation, alone and in combination with adsorption, also emulsion fractionation as means for renovating waste water for possible reuse. For example, one acceptable waste water purification process would produce water which contains 0.5 ppm or less of detergents and 0 ppm of other water soluble organic impurities. Such a product, after chlorination, may meet present drinking water standards. Of course, an acceptable purification process must provide high quality water at the lowest possible cost.

Foam fractionation of secondary effluent, obtained from the Bergen County Sewage Authority treatment plant at Little Ferry, N. J., removed about 95% of the detergents and 20-40% of the water soluble organic impurities. Similar results were obtained with waste effluents sampled at two other waste water treatment plants in New Jersey. The three plants chosen handle waste water which varies widely in industrial waste content, zero to 50%. In addition, synthetic sewage samples containing ABS detergents and proteins were studied. High removal of detergents was obtained consistently in either batch or continuous type foam fractionation columns. The conclusions from the work on the synthetic wastes seem to apply to the waste water effluents from the sewage plants. Thus, foam fractionation alone can produce

Source Of Waste Water Effluents	Type Of Effluent	------Initial Concentration------ Detergents ABS, ppm	Organic Impurities*, COD, ppm	% Removal ABS	% Removal COD
Little Ferry, N. J.	Secondary	2-8	50-200	95	20-40
Bernardsville, N. J.	Secondary	5	65	93	30
Sayreville, N. J.	Primary	5	750	79	5-10

75°F., 2" Diameter Column, 2.5 feet long, 63 x 10^{-3} SCF/Min. Air Flow Rate, Residence Time 3-5 Min.
* Water soluble impurities.

water which will meet the 0.5 ppm of detergents requirement, but it probably cannot purify water to 0 ppm of other water soluble organic impurities.

In the course of the foam fractionation study, the effect of variables such as pH, temperature, column geometry, drainage, gas rate, residence time, and additives were studied. Effective separations require at least 0.8 SCF of air per gallon of waste effluent. A liquid residence time of no less than 2.5 minutes and no more than four seems adequate for removing 95% of ABS and 20-40% of COD material. Certain surfactants such as traces of an uncharged detergent added after all the foam has been removed from the waste water brings up COD removal to 65%. More data, however, needed.

An attempt was made to develop a mathematical model for predicting the rate of disappearance of ABS from waste water during foam fractionation. The model seems to fit the data qualitatively.

A brief evaluation of emulsion fractionation shows that this process does not look promising for removal of the soluble organics from waste water.

A promising approach to give complete removal of soluble organic impurities is a carbon adsorption step after the waste water effluent has been foamed to remove detergents and other high molecular weight, very surface active materials. Removal of high molecular weight compounds by foaming increased the adsorption capacities of activated carbon because these materials probably block pore openings and decrease the carbon surface available for adsorption. For example, adsorption capacities were 6 to 30% higher for foamed than for unfoamed secondary effluents. Also, in several runs, the foamed and carbon treated secondary effluents contained 0 ppm of organic impurities (COD). Therefore, foam fractionation in combination with carbon adsorption is a method for purifying waste water.

The costs of the foam fractionation process were estimated for small size plants (108 thousand, 1.08 million GPD) and large size plants (10.8, 54 and 108 million gal./day). The small capacity plants can probably handle small industrial waste systems, while the larger plants can handle effluents from waste water treatment plants. The operating costs for processing waste water to make a 0.5 ppm ABS product from a feed containing 2 to 7 ppm ABS is about 2.5 and 1.5¢/1000 gal. for 10 and 100 million GPD plants, respectively.

Over-all, foam fractionation looks like a feasible and low cost process for removal of soluble organics from waste water. It is most effective for removal of synthetic detergents. Future work should look into: the effect of additives for more complete COD removal, analysis of the foam phase to determine the nature of the organics concentrated in the foam, dynamic analysis of the foaming process to establish the response of the system to sudden rise or drop of organics in the feed and methods of handling such changes, methods to reduce the liquid rejected as foam, and to dispose of the foam.

II. INTRODUCTION

The rapid growth of population, together with the threat of over-draught of readily available water supplies, makes it imperative that all possible avenues be explored to improve water conservation and reuse practices. The reuse of water is now a reality in some areas; eventually reuse will become an accepted and necessary practice in most densely populated areas of the United States. In the area of reuse of treated sewage effluents, considerable progress has been made. Present methods of waste treatment, however, cannot cope with this growing problem. Research under the Advanced Waste Treatment Program of the U.S. Public Health Service is being undertaken to evaluate physical and chemical principles applicable to the removal of contaminants from water.

Some of the most important contaminants in waste water are soluble compounds, mostly organic in nature from commercial and industrial operations and from household detergents. These chemical pollutants create a problem because of the inability of existing sewage treatment processes, specifically, bacterial decompostion, to remove them effectively. As a result, they may add up in sufficient quantities to make drinking water unpleasant.

Many of the soluble organics are difficult to capture and identify, and they cannot be removed effectively by current treatment methods. The most spectacular substances are those characterized by foaming.

A logical approach to the removal of dissolved organics which produce foaming is by the use of foam fractionation. This technique has been used in hydrocarbon as well as in aqueous systems and has successfully separated some of the metal contaminants from petroleum (1), as well as fractionated complex, heat-sensitive protein materials from aqueous systems (2).

Because of wide spread interest in separating soluble organic compounds in waste water, an evaluation of the foam fractionation process was undertaken by the Esso Research and Engineering Company under contract No. PH-86-62-26 from the U.S. Public Health Service.

Exploratory studies have shown that only crude applications of this technique can remove as much as 85% of the alkyl benzene sulfonates from secondary sewage effluents (3). In addition, approximately 10% of the other organic pollutants present have been removed.

Foam Fractionation Investigated For Removal Of Soluble Organics From Waste Water

A water soluble organic molecule contains a water soluble group as well as a hydrocarbon soluble group. The hydrocarbon soluble end of the molecule will have little attraction for water, and there will be a tendency for it to accumulate at the surface of the aqueous solution. Such molecules are known as surface active, will exert a surface pressure and lower the surface tension of the pure water. Foam fractionation takes advantage of the surface activity of the soluble organics in water by providing a practical means for their separation. By creating large liquid-gas interfacial areas, as exists in foams, and then removing this "foam phase" from the surface of the bulk liquid, remarkable separations of surface active impurities from water may be obtained. The concentration in the foam will be greater than in the residual liquid ("foamate") or the original solution ("feed").

Foam Fractionation Studied In Combination With Adsorption

Foam fractionation may not remove the low mol. wt. organics which are weakly surface active. These may, however, be removed by a subsequent step in which the residual liquid from foam fractionation is passed over a bed of activated carbon. In the absence of high mol wt. soluble organics, already removed by foam fractionation, the adsorption bed capacity may be larger because the high mol. wt. organics which may plug the carbon pores have already been removed.

Emulsion Fractionation Investigated For Removal Of Soluble Organics

Emulsion fractionation is another technique which was evaluated for removal of the soluble organics from water. Ordinarily, this technique provides a means of separating from organic liquids which are immiscible with water (e.g., hydrocarbons) soluble compounds which are active at the liquid-water interface; i.e., interfacially active compounds. When such a liquid is emulsified with water, these active compounds will migrate to the interface or emulsion layer. When the emulsion is partially broken, the concentration of the active compounds will be greater in the emulsion phase than in either the liquid or water phases.

It is conceivable, that based on the principles described above, that if water contaminated with soluble organics is emulsified with a pure hydrocarbon phase such as benzene or a petroleum naphtha, the surface active molecules in the water will be transferred to the emulsion layer. When the emulsion is partially broken, the concentration of the active compounds will be greater in the emulsion phase than in either the water phase or the organic phase.

Scope Of The Work

Foam fractionation alone and in combination with adsorption, as well as emulsion fractionation were evaluated for separation of organics from waste water. The objectives were to:

- Determine the extent of removal of ABS and COD by foaming alone.
- Define the effect of the operating conditions (e.g., gas requirement, gas flow rate, column geometry, temperature, pH, gas bubble size) on removal of ABS and COD by foam fractionation.
- Determine, based on the data obtained above, the cost of water treatment by foam fractionation.
- Determine the effect of prefoaming on carbon adsorption capacity and concentration of ABS and COD in effluent from the combination steps.
- Explore briefly the potential of emulsion fractionation for removal of the soluble organics.

It must be emphasized that this investigation was made to determine the feasibility of removing detergents and other water soluble organics from waste water by foaming. Accordingly, many different variables which might affect the removal by foaming were screened. The purpose was to determine quickly those variables which are important and which must be controlled to obtain essentially complete removal of detergents and water soluble organics from waste effluents. Therefore, no extensive study has been made of any one variable.

III. SOURCE OF WASTE WATER EFFLUENTS

Samples of waste water effluents were obtained from three different waste water treatment plants in New Jersey.

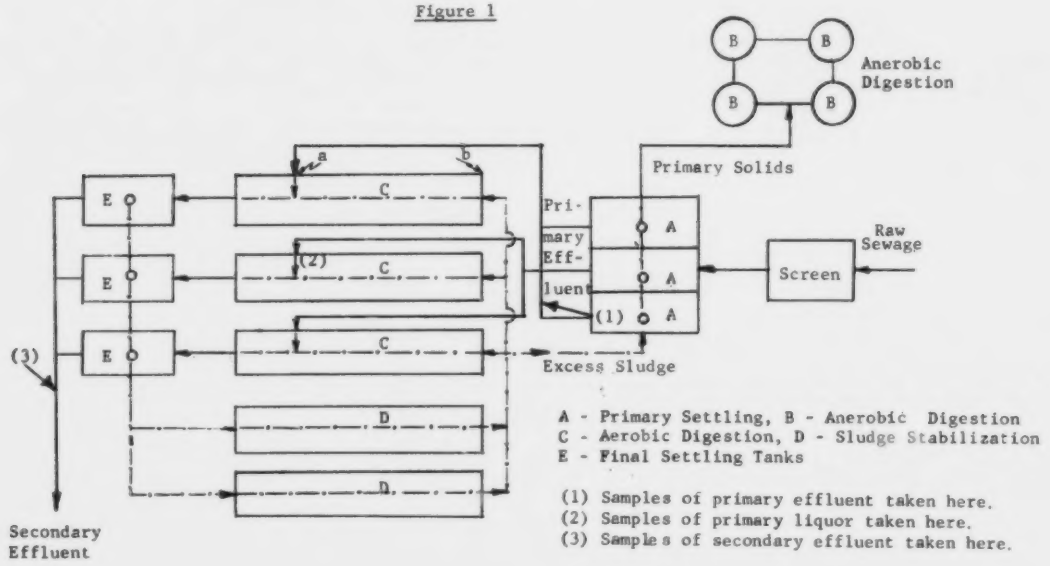
Bergen County Sewage
Authority Waste Treatment Plant

Most water effluents used in this study were obtained from the Bergen County Sewage Authority waste water treatment plant at Little Ferry, New Jersey. This plant is designed to handle 20,000,000 gallons/day of waste water, but it is presently overloaded and is treating up to 50,000,000 gallons/day. The plant is now being expanded to handle these larger volumes and construction is under way. The Bergen County Plant serves about 350,000 people in 28 municipalities. Most of these communities have some industries. The plant also serves five industries directly. These are: four pulp and paper industries and one intermediate dye and chemical industry. These five industries contribute about 3-4,000,000 gallons/day of waste water. The average total waste water volume is about 40,000,000 gallons/day.

It is not possible to estimate how much industrial wastes come from each of the 28 municipalities. There are certain complicating factors. For example, one town had a night population of 23 people and a day population of a little over 10,000 because of a large industry in this town. This is not, however, a typical example of the type of municipality served by this waste water treatment plant.

A schematic diagram of the Bergen County Sewage Authority waste water treatment plant at Little Ferry, N. J. is shown here. The locations in the plant where samples of waste water were taken are shown by the numbers 1, 2 and 3. The secondary treatment step in this plant is an activated sludge treatment process.

Figure 1



Preceding page blank

Waste Water Treatment
Plant In Bernardsville, N. J.

The waste water treatment plant in Bernardsville, New Jersey, handles only domestic wastes and serves a community of about 10,000 people. It has primary and secondary treatment processes. The secondary treatment step is an activated sludge treatment process. The secondary effluent is generally chlorinated.

Middlesex County Sewage
Authority Waste Treatment Plant

Foaming experiments were also conducted using primary effluent which was obtained from the Middlesex County Sewage Authority Plant at Sayreville, New Jersey. This plant has only a primary treatment process and the waste effluent is finally discharged into the ocean at the Raritan Bay. The plant treats both domestic and industrial wastes, and the industrial wastes may amount to about 50% of the total.

Problems Connected With
Variation Of Waste Water

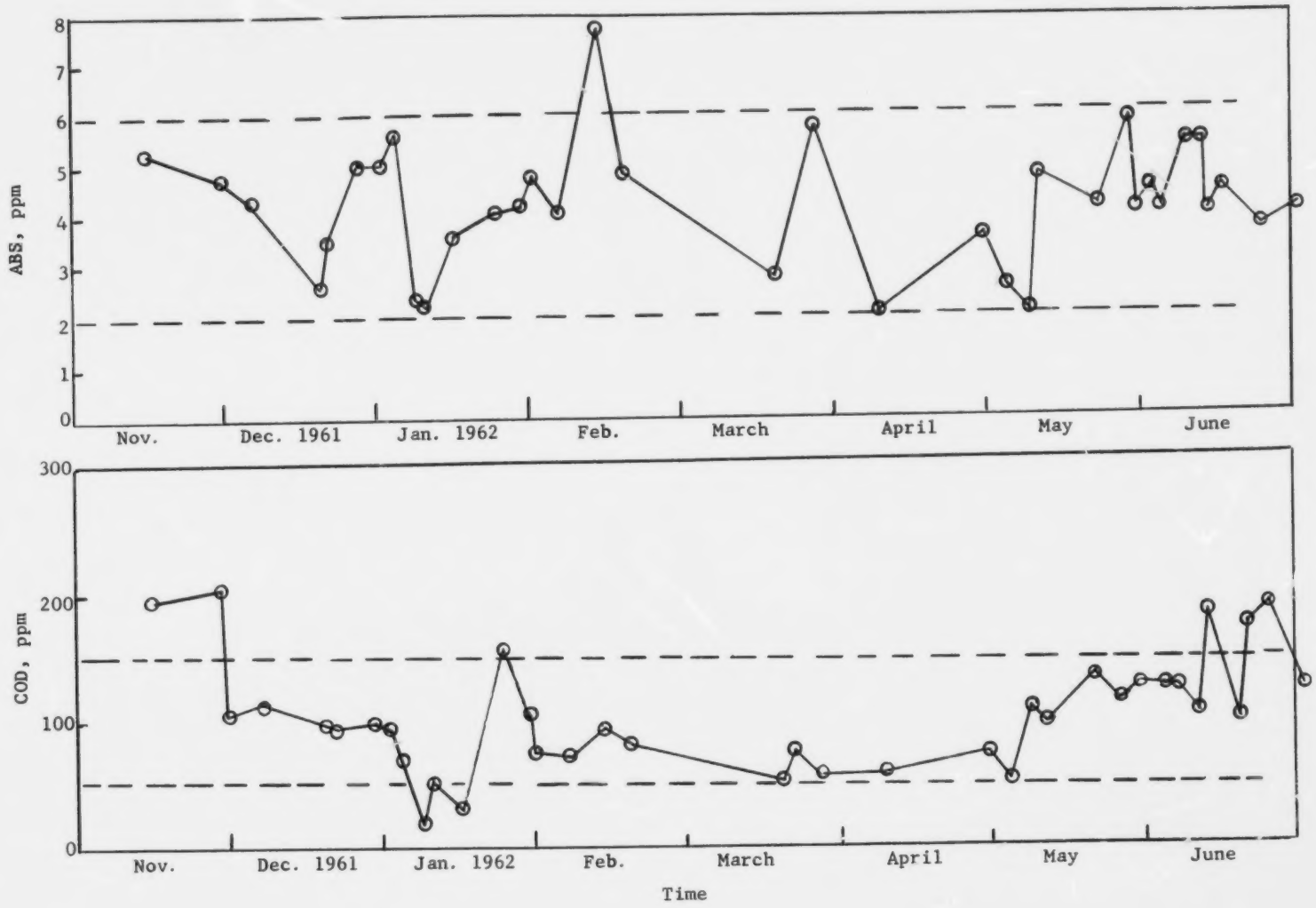
One of the main problems with which this research effort has been plagued with is the variation of the samples composition. As shown from the companion Figure 2, the ABS content varied from 2 to 7.5 ppm, the COD also varied from 20 to 200, more detailed data are shown in Appendix Table 1. In sewage plant effluents the volume of the foam does not necessarily depend on the ABS concentration. For example, to remove 2 ppm of ABS, just as much foam may be discarded as to remove 7 ppm of ABS. This is attributed to the interactions between ABS and other soluble organics such as proteins. This interaction, its causes and effects, will be discussed later in this report.

Since the samples collected could not be stored for more than 36 hours, only a limited number of experiments could be carried out on any batch obtained from the waste water plant. Storage time is limited to avoid any degradation of organics whose disappearance may be confused as having been removed by foam fractionation. To cope with this problem, efforts were made to study with one batch, a range of values within one variable. To study another variable, however, it was necessary to obtain another batch of waste water.

In most cases, however, the ABS content from the Bergen County Sewage Plant was between 2-6 ppm, and the COD varied between about 50-150 ppm.

Figure 2

RANGE OF VARIABILITY OF ABS AND COD IN SECONDARY EFFLUENT
FROM BERGEN COUNTY SEWAGE AUTHORITY TREATMENT PLANT AT LITTLE FERRY, N. J.



IV. ANALYTICAL PROCEDURE

The surface and interfacial tension of waste water effluents were measured by using a du-Nuoy ring tensiometer (1).

Foam stabilities of the waste effluents were measured by shaking 50 cc. of waste water solutions in a 100 cc. graduated cylinder for 30 seconds at a uniform rate (about 4 ft./sec.). The time for the foam to collapse is the measured foam stability. High values (> 5 min.) indicate good foam stability and low values (< 1 min.) indicate poor foam stability.

Foam volumes were measured during each foam stability test described above. The foam volume was that volume of foam which remained on top of the liquid after the shaking was stopped.

Alkyl benzene sulfonates (ABS) in the waste water effluents were determined by the methylene blue method (2).

The waste water effluents were also analyzed for chloride ion, chemical oxygen demand (COD), total dissolved solids (T.S.S.) and volatile solids (V.S.) by the standard methods (2). All COD values reported here have been corrected for the chloride ion content of the waste water effluents.

In several series of experiments, solutions containing various detergents and egg albumin were added to waste water or distilled water to determine their effect on foaming. In most cases, these solutions were prepared by dissolving 1.0 gram of additive in distilled water in a 1000 cc. volumetric flask. Aliquots of these stock solutions were then added to waste water effluents in different experiments.

Waste Water Effluents Filtered Before Foaming

ABS and COD measurements were made on nonfiltered, filtered, and centrifuged primary and secondary waste effluents from the Bergen County treatment plant. The purpose of these measurements was to determine if filtration through Whatman No. 5 filter paper, a pretreatment step carried out prior to foam fractionation, removes appreciable quantities of water soluble organics by adsorption. Adsorption by filter paper of water soluble organics from waste effluents would increase the removal of these materials more than expected by foam fractionation alone.

Effluent And Treatment	Batch	ppm COD	T.S.S.	V.S.	ABS
Secondary Effluent					
Unfiltered	A	201	81	64	4.7
Filtered	A	101	5	5	4.7
Unfiltered	B	108	40	26	5.0
Centrifuged	B	98	13	5	5.2
Primary Effluent					
Unfiltered	C	133	61	41	2.0
Centrifuged	C	101	20	14	2.3

T.S.S.- Total suspended solids.

Preceding page blank

Paper filtration did not decrease the ABS content. This is probably understandable because approximately 1000 cc. of effluent are usually filtered through in a batch operation. Thus, any adsorption of ABS by the filter paper would be difficult to detect in 1000 cc. of effluent. In a normal run, 1200 cc. of waste water are passed over a single filter paper.

Centrifugation, also, did not decrease the alkyl benzene sulfonates because they are soluble in water.

COD content was, however, reduced either by centrifugation or filtration. This reduction is due to the removal of solid particles which contribute to a major portion of the COD.

The solids in the effluents from the Bergen County Sewage Authority Plant are high because of the insufficient settling tank capacities either for the primary or secondary effluents. This situation is now being remedied at the plant by providing additional settling tanks now under construction.

Based on the qualitative and quantitative data, that filtration does not remove ABS, waste water effluents were filtered through No. 5 filter paper prior to foam fractionation. Filtration was preferred to centrifugation because it is easier to carry out in the laboratory and is more adaptable to inclusion in the sewage treatment plants.

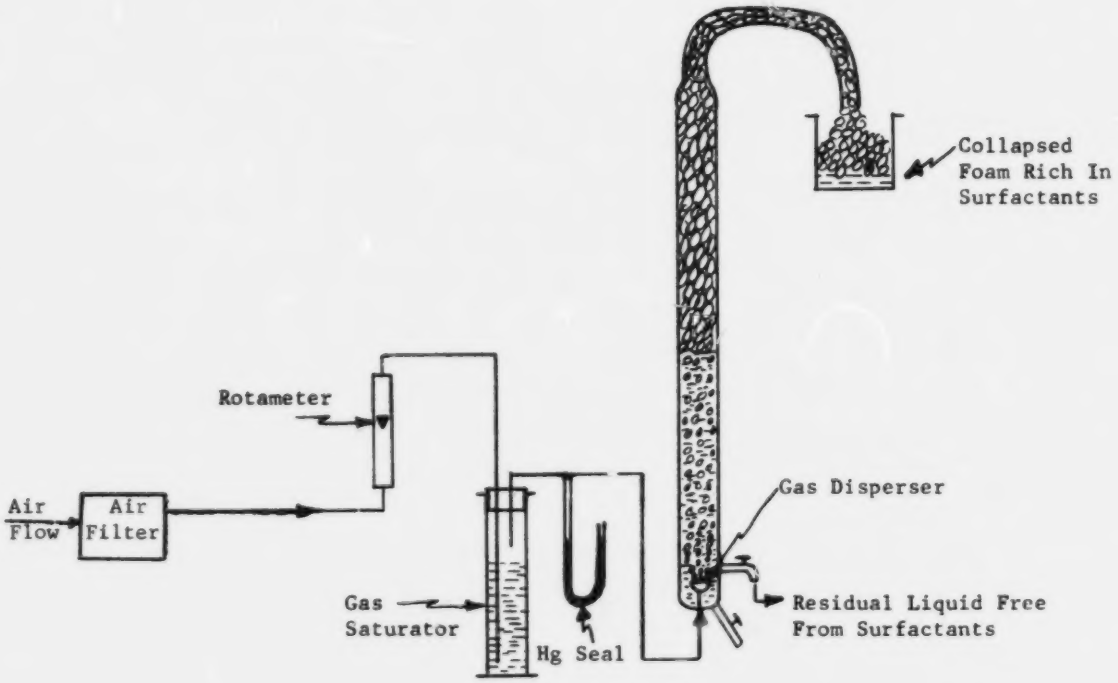
V. FOAM FRACTIONATION STUDIES

A. Equipment And Procedure

Batch Equipment And Procedure

The foam columns used in the batch operation consist of a glass tube of 3/4" to 2" in diameter and 2.5 feet high. Gas is metered by a rotameter, it is then saturated with water and introduced into the column through a fritted glass gas disperser (see Figure 3).

Figure 3



A premeasured batch of water is introduced to the column. Gas is then introduced and foam starts to form and rise above the liquid level. The foam phase is passed overhead and collapsed. In the batch runs, foam is collected until no more foam can be recovered in the foam receiver. A sample of the liquid is then withdrawn before the foam in contact with the liquid surface is collapsed. The volume of the collapsed foam phase is then measured. This volume is used to determine from other calculations to be described later the ratio of the surfactants concentration in the foam to that in the liquid.

Continuous
Equipment And Procedure

Foam fractionation experiments were made using continuous units. These runs were made in columns which were either 2" or 4" in diameter and 3 feet long. Filtered secondary effluent was pumped into the column at the mid-point and relatively pure, foamed, water was pumped out at the bottom of the column. The foam was collected overhead in graduated cylinders. The flow rates of secondary effluent into the column and foamed effluent out of the column were controlled by using two liquid rotameters. During a run, the liquid height in the column was maintained constant to about $\pm$ 1 inch. The air was saturated with water before it was introduced at the bottom of the foam fractionation column through a filtered glass filter. The foam was removed from the column at various distances from the liquid interface.

Samples of foamed water were withdrawn periodically from the outlet line for ABS and COD analysis. The foam overhead was segregated into small volumes during the runs and then submitted for ABS or COD analysis (see Figures 4, 4A, 4B and 4C).

Criteria Used To
Interpret Results

Three criteria were used to interpret the results. These were:

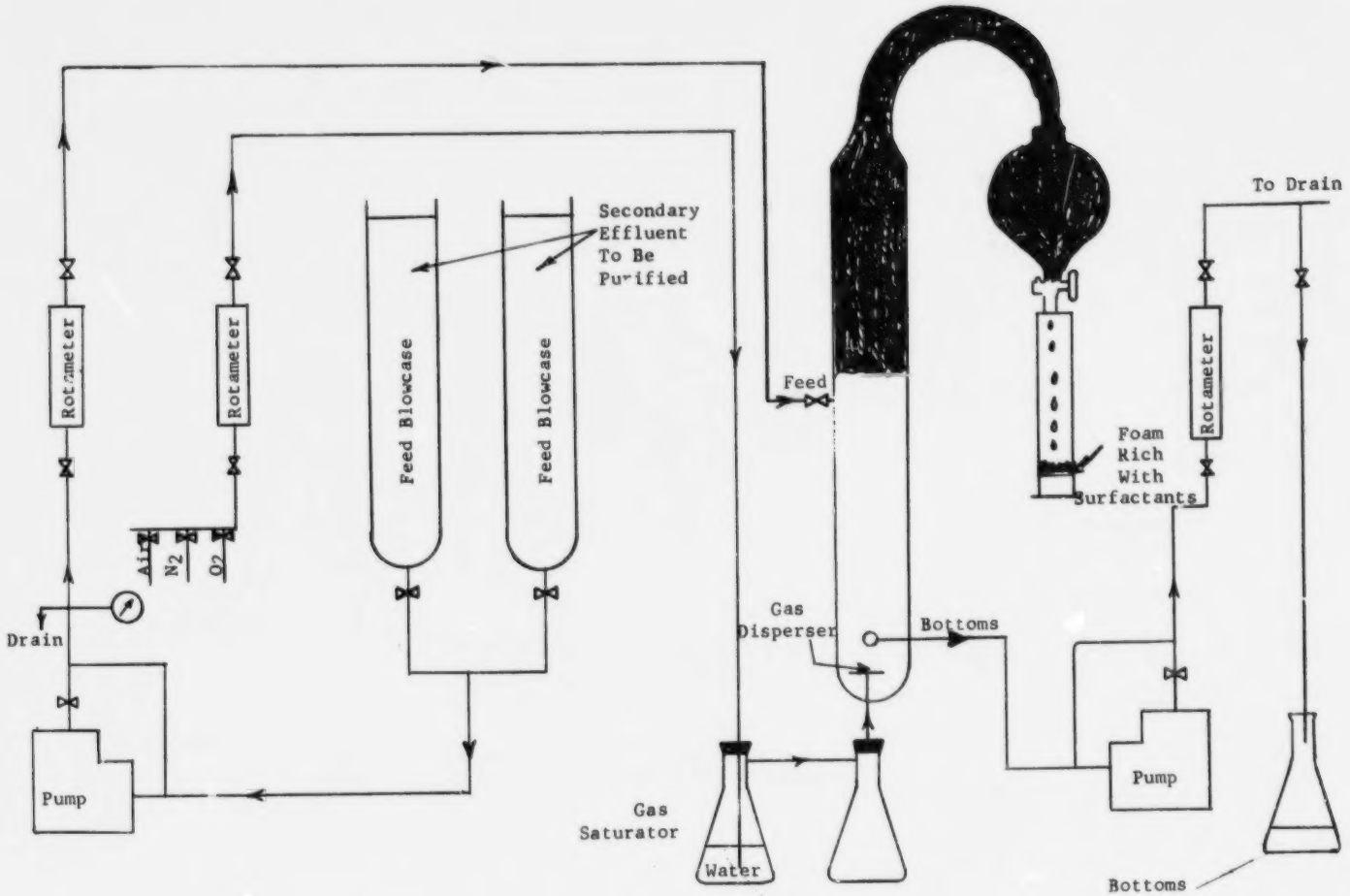
- The percentage removal of ABS or COD. The values show the maximum removal which can be obtained and it is based on the concentrations of ABS or COD.

- The ratio of the concentration of the surfactants in the foam to that in the residual liquid, C_F/C_L. This ratio indicates that effectiveness of foam fractionation. High ratios show that foaming is successful, and that a small amount of water will be collected as collapsed foam; the reverse is true for low ratios. It is important to obtain a foam phase very rich in surfactants in order to reduce the size of the facilities needed either for recovery or disposal of surfactants concentrates. A sample calculation for the ratio C_F/C_L is shown in Appendix Table 2. This quantity has been calculated only for solutions of synthetic detergents in distilled water.

- The volume of collapsed foam is used to indicate the effectiveness of foaming to concentrate the ABS and COD in a small amount of liquid.

Figure 4

CONTINUOUS FOAM FRACTIONATION UNIT



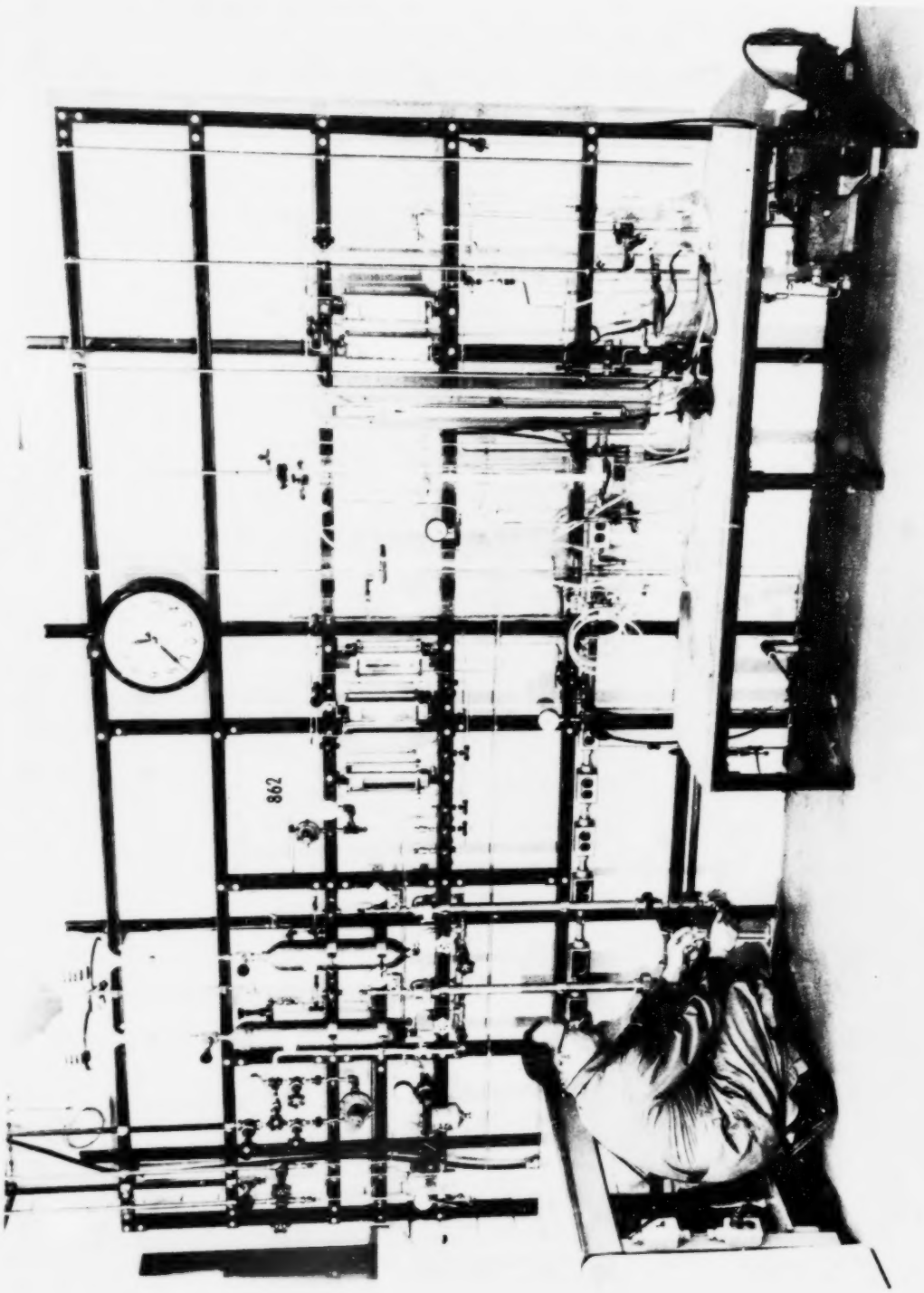


Figure 4A

Figure 4B

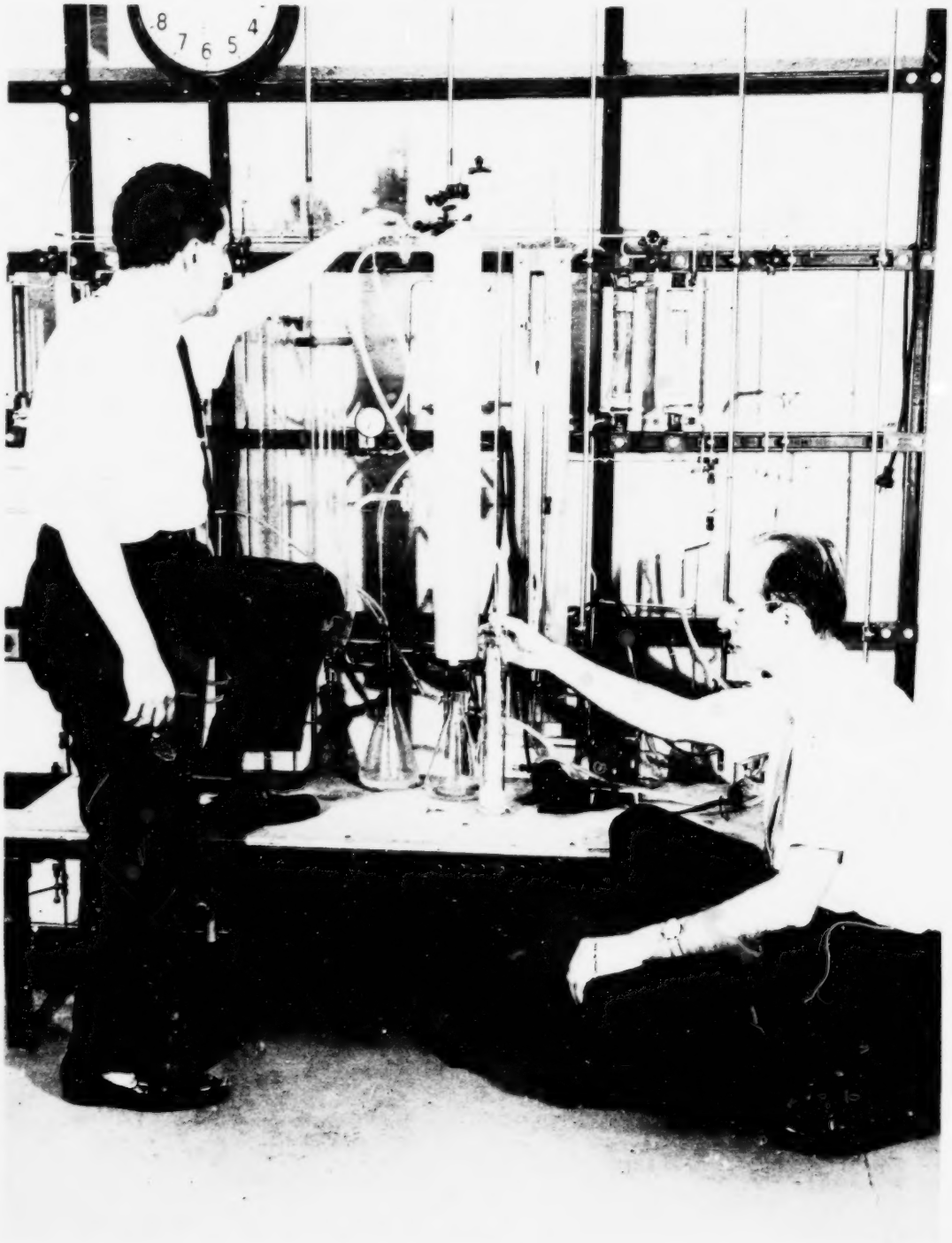
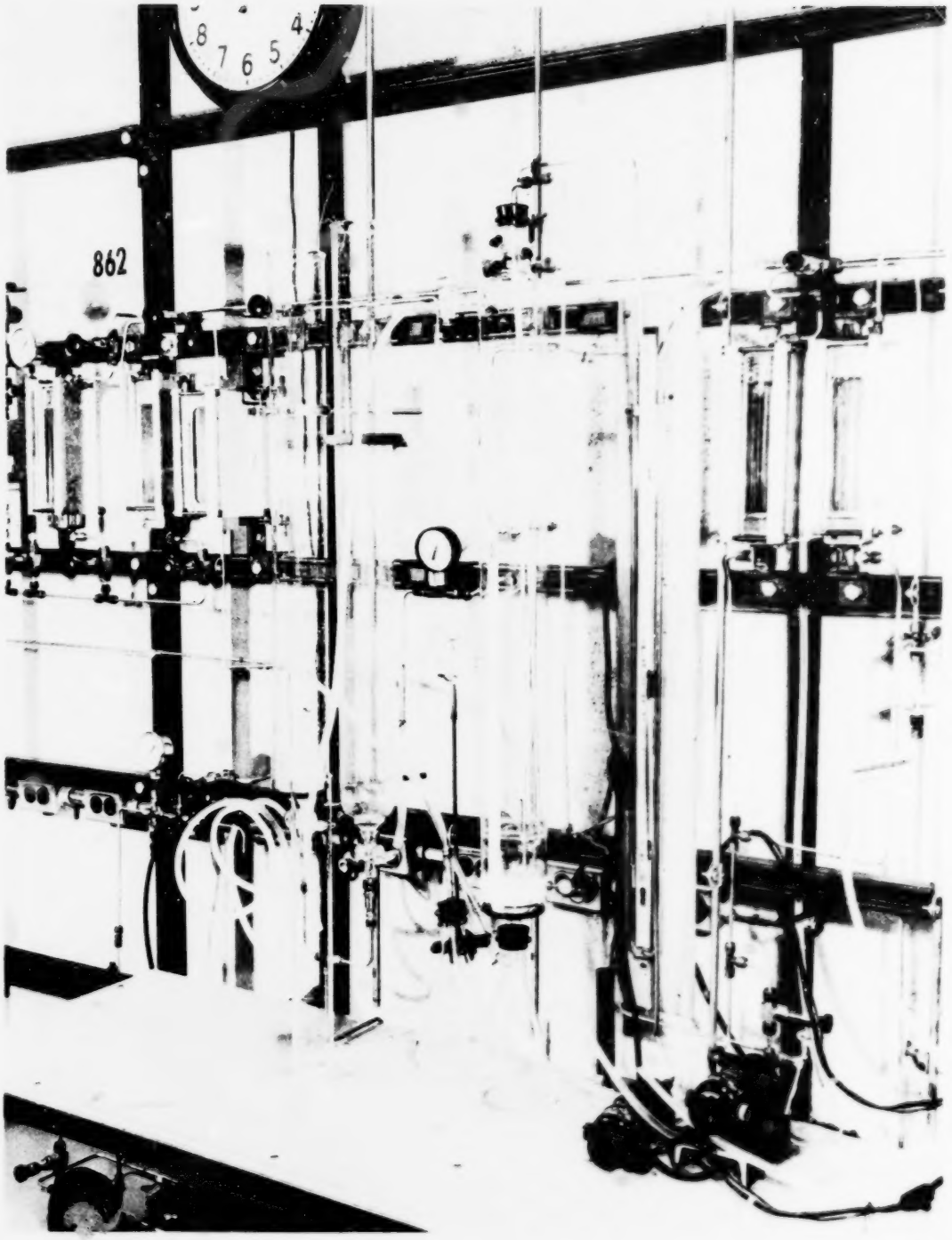


Figure 4C



B. Batch Foam Fractionation

Both Primary And Secondary Effluents Were Foamed

Batch fractionation runs were made using primary and secondary effluent. These experiments were made to indicate the most desirable location for a potential foam fractionation step in a waste water treatment plant. The foam fractionation runs were made in a 30" glass column, 2" in diameter, using a fine size gas disperser (see Appendix Table 3 for more complete experimental details).

Run No.		% Of Feed Collected As Foam	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Sec. Eff.	U	-	157	4.72	-	-
			------Products-------			
7	U	7.9	100	0.4	27	92
10	F	10	69	0.1	49	98
Primary Eff. (Tank)	U	-	451	1.8	-	-
			------Products-------			
8	U	1.2	353	0.6	22	67
12	F	1.6	192	0.3	58	83

Temp., 78°F.
U - unfiltered, F - filtered.

The data indicate that detergents (ABS) can be removed to approximately the same low concentration, 0.1-0.3 ppm, from the two effluents. However, the lowest chemical oxygen demand values (COD) were obtained with secondary effluent.

Comparison of runs using filtered and unfiltered effluents indicates that suspended solids can contribute to extremely high COD values. For example, COD was reduced from 451 to 353 ppm by foaming unfiltered effluent, while it was reduced from 451 to 192 ppm by foaming and filtering the effluent. For a water renovation process, foam fractionation will probably be most suited to treat the secondary effluent since the aeration and settling in the plant do a major part of COD reduction and foaming can be used as a finishing step.

Foam Fractionation Effectiveness Depends To Some Extent On Gas Bubble Size And Column Diameter

Experiments were made to determine the effect of gas bubble size on removal of ABS and COD. A foam phase containing small gas bubbles has a larger interfacial area than a foam phase containing large air bubbles if the air volume is the same. This increased interfacial surface area per unit volume of air should enhance the removal of surface active materials since surfactants tend to concentrate at a gas-liquid interface.

To study the effect of gas bubble size, distributors of different porosities were investigated. In these experiments, the column diameter was also varied using the same gas distributor.

The data suggest that at the same column diameter, more COD is removed with a fine gas disperser than with a medium gas disperser, 28% vs. 21% for both the 3/4" and 2" columns. The trend is the same for the ABS removal. More complete data are shown in Appendix Table 4.

Run No.	Col. Diam.	Gas Disperser	% Of Feed Collected As Foam	ppm COD	ppm ABS	% Removal COD	% Removal ABS
		Feed	-	113	4.3	-	-
		Prod.					
24	3/4"	Med.	0.22	89	1.3	21	70
25	3/4"	Fine	0.22	81	1.2	28	72
22	2"	Med.	0.08	89	0.9	21	79
26	2"	Fine	1.0	81	0.6	28	86

Within the range of column diameters studied, varying the column diameter does not seem to have any large effect on the per cent COD removed. This applies when either a medium or fine gas disperser was used, and the column diameter varied from 2" to 3/4". Per cent ABS removal appears to depend on column diameter, however. Slightly more ABS was removed with a 2" or 1-1/2" column diameter as compared to a 3/4" column diameter. This could be explained by the observation made that small gas bubbles tend to coalesce more readily to form larger gas bubbles in narrow diameter columns, thereby reducing the interfacial foam area. It is also possible that in narrower columns, drainage of liquid from the foam phase is difficult, thus making separation less efficient. However, more experiments are needed to establish the effect of column diameter more precisely, especially using the same ratio of air to liquid foamed.

Run No.	Col. Diam.	% Of Feed Collected As Foam	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed						
Sec. Eff.	-	-	113	4.3	-	-
Products						
22*	2"	0.08	89	0.9	21	79
23*	1-1/2"	0.1	129	0.8	-	81
24*	3/4"	0.22	89	1.3	21	70
25**	3/4"	0.22	81	1.2	28	72
26**	2"	1.0	81	0.6	28	86

* Medium gas dispersers.
** Fine gas dispersers.

Foam Fractionation Removes
Soluble Organics Other Than ABS

The preceding data also indicate that water soluble organics other than ABS are removed by foam fractionation from secondary waste effluents. The following table summarizes the pertinent data.

	ppm			
Run No.	COD	ABS	COD Due To Contaminants Other Than ABS	Organics Removed, Other Than ABS
Feed-Sec. Eff.	113	4.3	104	-
Products				
22	89	0.9	87	16
24	89	1.3	86	17
25	81	1.2	79	25
26	81	0.6	80	24

The COD values due to contaminants other than ABS have been determined by substracting from the ppm of COD in a sample twice the ppm of ABS. This technique assumes that 1 ppm of ABS is equivalent to 2 ppm of COD (3). Differences in COD values, which have been corrected in this manner, indicate the amount of water soluble organics other than ABS which have been removed by foam fractionation. As much as 25 ppm of soluble organics other than ABS are removed during the foaming experiments. Apparently, the presence of detergents provides stable foams with sufficient interfacial area to remove the non-ABS soluble organics.

A Major Part Of ABS Is Removed
In Initial Fraction Of Foam Overhead

Experiments were made to determine the effect of air flow rate on the removal of ABS and COD materials and the volume of liquid rejected as foam. The experiments were made using 450 cc. of filtered secondary effluent in a 3/4" column with a "fine" gas disperser. The data indicate that both ABS and COD removal tend to increase with air flow rate. However, with increased gas flow rates more liquid is rejected as foam (Figures 5 and 6). The amount rejected as foam is not proportional to the extents of removal. For example, in these particular experiments 88% of the ABS, and 28% of the COD were removed in 0.7% of the feed rejected as foam. With rejection of more foam only very small additional removals were obtained. For example, ABS removal increased from 88% to 91% when the air flow rate was increased from 32.8×10^{-3} to 70.4×10^{-3} SCF/min. (Appendix Table 5).

COD removal appears to depend more on air flow rate than ABS, although the bulk of it is still removed with the first material rejected overhead. These runs were made all on the same day. The results obtained here indicate only general trends and more work is required in this area.

Run No.	Air Flow Rate CF/Min. STP x 10^3	Foam Overhead Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed						
Sec. Eff.	0	-	113	4.3	-	-
Products						
18	20.5	0.7	81	0.5	28	88
19	32.8	3.5	73	0.4	35	91
20	45.5	4.9	73	-	35	-
21	70.4	5.3	65	0.4	42	91

Figure 5

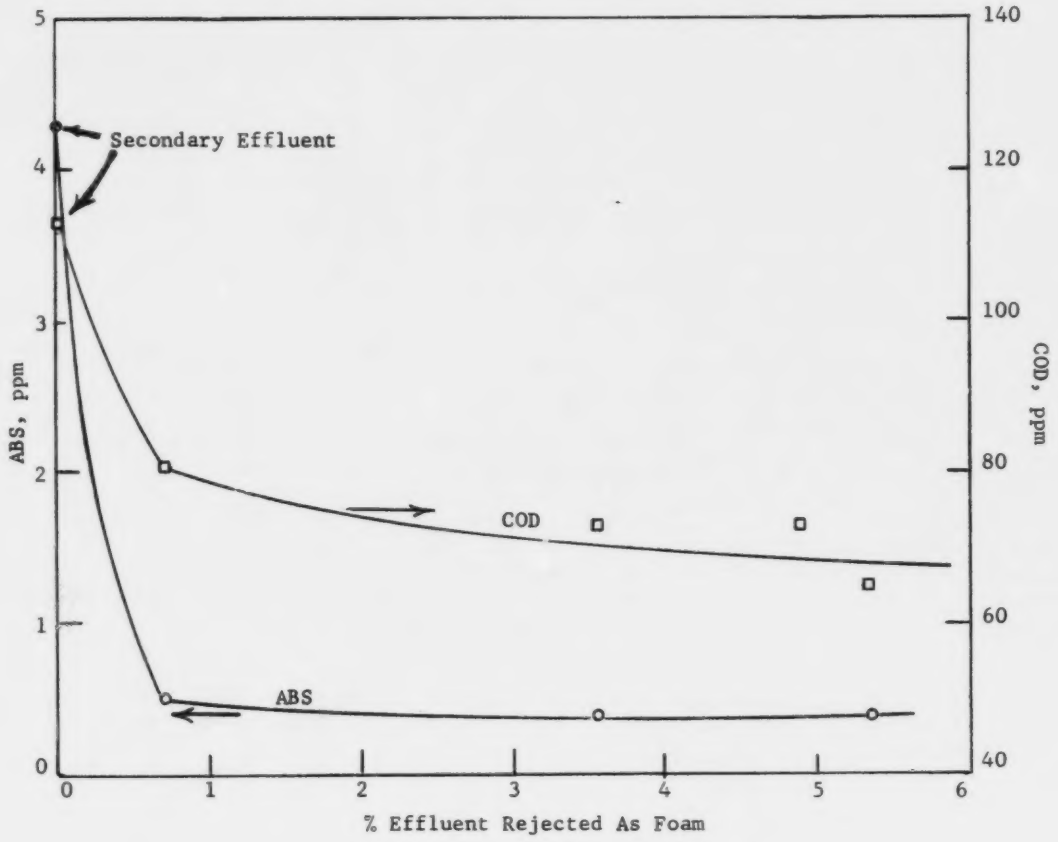
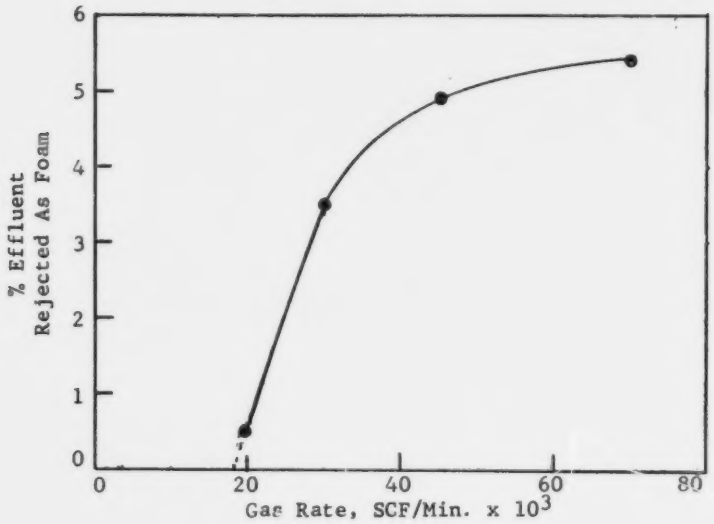


Figure 6



Temperature Effect Appears
To Be Small Over 35-75°F. Range

From earlier work it has been shown that foam stability and volume are known to depend on temperature (3). Foam persistence or stability is usually less at higher temperatures; however, depending on the surfactant concentration, increased temperature can either decrease or increase foam stability. From theoretical considerations, the Gibb's equation:

$$\Gamma = -\frac{C}{RT}\frac{d\gamma}{dC}$$

where Γ = excess of solute per unit of surface area, moles/sq. cm.
C = concentration of solute moles/sq. cm.
R = 8.3×10^7 dyne cm./mole °K.
T = absolute temperature, °K.
γ = surface tension dynes/cm.

predicts that at lower temperatures, the surface excess concentration of surface active materials, Γ, should increase. Therefore, at lower temperatures, foam fractionation should remove more surface active materials if the same amount of more foam phase is generated. This is true because separation by foam fractionation depends on the interfacial surface area of the foam phase as well as on the surface excess concentration, Γ, (2). These considerations suggested that temperature is an important variable in foam fractionation. Therefore, foam fractionation runs were made using secondary effluent at 75 and 35°F. These runs were made using secondary effluents which were sampled on different days. The foam fractionation runs were made using a 2" diameter column, a fine gas disperser, and 1200 cc. of secondary waste water effluent. Detailed results are shown in Appendix Table 6.

From the limited data available it appears that removal of soluble organics at 35°F. is not as effective as at 75°F. In both series of runs, less ABS was removed at the lower temperature. Also, COD removal was less in one run and unchanged in another at the lower temperature. The greatly decreased ABS and COD removal in one case (15 U) is undoubtedly due to the small foam phase and the decreased interfacial surface area. In the other series of runs (54 and 57 F), slightly more foam phase was collected at 35 and 75°F., and the changes in ABS and COD content are not as great. These data emphasize the difficulty in obtaining the effect of different variables on foam fractionation when working with such complex mixtures as secondary waste water effluents.

Short Residence Times Are Sufficient To Remove Most Of The ABS

A series of runs were made to determine the effect of aeration time on ABS and COD removal. Aeration times in the range of 4 to 10 minutes were tried.

Run No.	Time, Min.	Foam Overhead, Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.	-	-	92	7.70	-	-
72	4	15.4	72	0.64	22	92
73	6	16.6	53	0.69	42	91
74	10	17.1	88	0.40	4.4*	95

* Unusually low COD removal was obtained. This is attributed to an error in sample analysis. Most COD removals vary between 20-40% in this report.

The data indicate that residence times in the range of 4 minutes are adequate for almost complete removal of the ABS (92%). Somewhat higher removal of the COD was obtained with longer aeration times (4 to 6 minutes), although the data are not firm.

These short residence times indicate that foam fractionation columns of reaonsable size can probably be used for continuous operations (Appendix Table 7).

Variation Of pH Studied To Improve Removal By Foam Fractionation

Various foam characteristics are known to depend on the solution pH. For example, it has been demonstrated that the foam of a solution of protein bovine serum albumin exhibited maximum enrichment at the isoelectric pH at which point the protein exhibited highest surface activity. Enrichment fell off with either increasing or decreasing pH (4).

It is recognized that altering pH to remove certain surfactants may not be practical for treatment of sewage effluents. A study, however, aimed at understanding what can be and cannot be enriched in the foam at pH 7 and at higher or lower values was undertaken.

Effect Of pH On
Foaming Of Secondary Effluent

Foam fractionation runs were made using sulfuric acid or sodium hydroxide to alter waste water effluent pH.

COD analyses of secondary effluent with added NaOH or H_2SO_4 indicate that COD content is increased also in this case. However, this is probably indicative of reproducibility of the COD analytical procedure, since NaOH or H_2SO_4 alone should not increase COD content (5). Seventy eight ppm (average value) was used as feed COD content in subsequent calculations. Increasing the pH from 7.2 to 11.7 has no effect on the final COD content, always 50 ppm. The ABS removal is slightly less at pH 9.9 or 11.7, but this is probably not significant because of the low final ABS concentration in these runs. Altering secondary effluent pH to 2.3 increases both COD and ABS removal, but the foam phase increases also, and this is undesirable. More complete data are shown in Appendix Tables 6 and 8.

Run No.	Foam Overhead, Vol. %	pH	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.		7.2	71	5.6	-	-
Feed NaOH Added		10.1	82			
Feed NaOH Added		11.9	82			
54	15.0	7.2	50	0.09	36	98
55	14.3	9.9	50	0.14	36	98
56	21.6	11.7	50	0.14	36	98
Feed Sec. Eff.		7.4	20	2.28	-	-
Feed H_2SO_4 Added		2.3	35			
58	4.2	7.4	16	0.14	40	94
59	5.7	2.3	8	0.11	70	95

Because one effluent was used in the studies in the low pH range and another one on the high pH range, this brings in a factor which may complicate interpretation of the data. Therefore, additional work was carried out.

Best Data, Show Enrichment
Of ABS And COD In Foam Improved
At pH Higher And Lower Than 7

In these new experiments, the same secondary effluent was used for pH studies ranging from 2.1 to 11.9.

The data showed as some earlier data have, that the volume of liquid rejected as foam rich in surfactants is minimum at the neutral pH of 7.4 or 7. The COD and ABS removals are also minimum at pH 7.4, and increase with either increasing or decreasing pH. More complete data are shown in Appendix Table 9, Figure 5.

Run No.	pH	Foam Overhead, Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.	7.4	-	92	7.70	-	-
74	7.4	17.1	88	0.40	4.4	95
78	2.1	29.2	72	0.07	22	99
79	2.6	28.3	88	0.11	4.4	99
76	9.9	28.3	60	0.17	35	98
77	11.9	39.2	56	0.10	39	99
83*	2.5	1.2	96	0.07	-	99
81*	10.5	0	84	0.14	8.7	98

* Sec. eff. foamed first at pH = 7.4, then pH was altered.

Although the ABS removal (95%) is minimum at pH = 7.4, it may not be economically feasible to alter the pH to 2.1, for instance, just to obtain an additional ABS removal from 95 to 99%. Also, the amount of foam generated increased from 17 to 29% which would be undesirable. The same argument would apply to changing the pH from 7.4 to 11.9.

Scheme Of Foaming, Altering pH, Then Refoaming Does Not Improve Removal of ABS or COD

To take advantage of the desirable effect of pH lower and higher than 7 on removal of surfactants, the secondary effluent was foamed at pH 7, the foam phase was removed, and then the pH of the residual liquid was altered, and the liquid foamed again.

Since pH values in the acid and base range produce more foam than at pH 7, it was thought that a preliminary foaming step at pH 7 may remove most of the ABS in the minimum amount of foam. The residual liquid then can be purified further by changing the pH from 7. This pH change will affect only the minor amount of impurities left behind, and would not consequently produce as much foam as that produced had the original secondary effluent been foamed at pH values higher or lower than 7.

It was also thought that this procedure might change the foaming characteristics of the foamed effluent and lead to additional COD removal. Some typical results are given for runs 81 and 83, described in Appendix Table 9. The data indicate that very little additional foam phase is generated when pH is altered and the effluent foamed a second time. At pH 10.5 and 2.5, only 0 and 15 cc. of additional foam phase were generated. Also, no significant improvement in COD removal was observed in these runs. Additional work to establish the effect of pH on COD removal is needed before a definitive recommendation can be made on this point.

Additives In Low Concentrations May Improve COD Removal

Foaming experiments were made in which very low concentrations of additives were used. Furthermore, the additives were chosen such that there was some possibility that ion pairs could be formed. In these experiments the charge was foamed, the foam was collected and removed, then small concentrations of detergents of different charges on the organic part of this molecule were added to the residual liquid in order to create more foam. The detergents used as additives represent an anionic detergent (Duponol), a cationic detergent (Ethoquad), and an uncharged detergent (Tergitol). These detergents were added in small quantities until a measurable amount of foam phase could be collected overhead. Also, the foam overhead was withdrawn about 2" above the liquid surface.

Removing the foam phase close to the foamed liquid surface may permit removal of weak surfactants which are difficult to remove by foaming. This reasoning is based on the hypothesis that strong surfactants are removed easily by foaming, but weak surfactants enter the foam phase for short distances and quickly return to the bulk liquid as the relatively unstable foam collapses.

In limited tests, COD removals as high as 65% have been obtained by foaming in the presence of additives. Detailed data are shown in Appendix Table 10.

Run No.	Type Of Additive	Additive Conc., ppm	Foam Overhead Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Secondary Effluent Feed		-	-	54	2.84	-	-
130		None	1.1*	62	0.20	-	93
129		None	0.6*				
	Uncharged	16 (Tergitol)	0.5**	19	0.17	65	94
128		None	0.5*				
	Cationic	28 (Ethoquad)	1.9**	27	0.07	50	97
127		None	0.5*				
	Anionic	43 (Duponol)	0.7**	62	0.17	-	94

* 1200 cc. secondary effluent.
** 1000 cc. secondary effluent.

A similar study was made using a sample of different secondary waste effluent. In these experiments the foam was not skimmed off immediately at the surface of the foamed liquid but was allowed to rise and discharge from the column about 12" above the liquid surface. In addition to the use of detergents a fourth additive, a protein egg albumin was evaluated. Duplicate COD analyses were obtained in these experiments and the average values are reported below.

With this particular sample of secondary effluent, foaming in the absence of additives did not remove any COD material and ABS removal was unusually low too. The highest COD removal was obtained with added Tergitol of Solefonate, 38% COD removal. However, the final ABS content was greater with added Solefonate (0.99 ppm) than with added Tergitol (0.28 ppm). Detailed data are shown in Appendix Table 11.

Run No.	Type Of Additive	ppm Additive	Foam Overhead, Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Sec. Eff. (Feed)	-	-	-	69	2.06	-	-
136		None	0.3	76	1.53	-	26
138	Uncharged	None	0	-	-		-
		21 (Tergitol)	0.7	43	0.28	38	86
140	Cationic	None	0.04	-	-	-	-
		36 (Ethoquad)	1.0	69	0.10	0	95
139	Anionic	None	0.02	-	-	-	-
		21 (Duponol)	0.4	57	0.39	17	81
141	Anionic	None	0.3	-	-	-	-
		21 (Solefonate)	0.5	43	0.99	38	52
142	Protein	None	0.2	-	-	-	-
		76 (Egg Albumin)	0.3	71	0.16	-	92

In this series of experiments, as in the earlier ones, Tergitol, an uncharged detergent gave the highest COD removal. Similar high COD removal was obtained with Ethoquad in earlier experiments. In these tests, zero COD removal was obtained with Ethoquad.

The higher level of COD reduction in the series of experiments where the foam was removed from a point close to the foam liquid (Runs 127-130) surface may confirm the view that weak surfactants enter the foam phase for short distances and quickly return to the bulk of the liquid as the relatively unstable foam collapses.

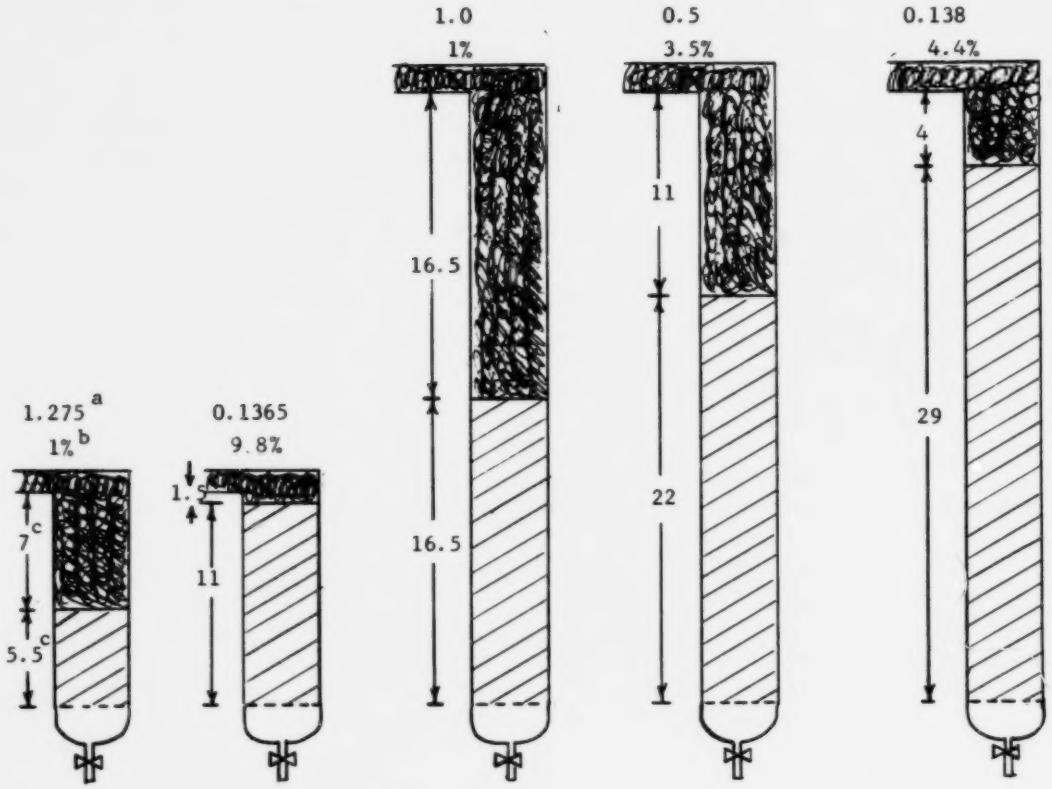
It is interesting to note that although added egg albumin did not enhance COD removal appreciably, it increased ABS removal from 26 to 92%. Adding proteins may be a practical technique to remove ABS from certain waste waters which are not improved by a simple foaming step, and the added protein should be more readily biodegradable than the ABS which it has replaced. Interactions between proteins and ABS will be discussed in another section of this report.

Good Foam Drainage
Reduces Volume Of Foam Rejected

Experiments were made in which the volume of the liquid in the foaming column was varied, also the height of the foam phase. The latter was controlled by withdrawing the foam at points which were at different distances from the level of the liquid. An illustration of the heights of the liquid to the foam are shown (see Figure 7).

The data indicate that the volume of foam rejected decreased when the foam column height is increased. This is logical because in a tall column the foam drainage is good and little liquid is carried out in the foam phase (see Figure 7, Appendix Table 12).

Figure 7



a) Height of foam to height of liquid.
b) % of liquid collected as collapsed foam.
c) Distances in inches.

Refoaming To Reduce Foam Reject
Cannot Be Carried Out Many Times

One of the principal questions asked about the foam fractionation process is the manner by which the collapsed foam rich in soluble organics will be ultimately disposed.

To reduce the cost of ultimate disposal, the amount of foam rejected should be as small as possible. One approach to do so is to refoam the collapsed foam as many times as feasible until a phase very rich in surfactants is obtained. Some experiments were carried out to determine the feasibility of such an approach.

Judging by the limited data obtained so far, it was found that enrichment in the foam phase C_F/C_L decreased with increased ABS in the liquid. With the secondary effluent containing 3.56 ppm ABS, C_F/C_L was 145 and the volume of the foam collected was 3% of the charge. When the collapsed foam was treated again, the enrichment ratio fell from 145 to 12, and the foam reject was 73% of the feed to the second foaming step. A third foaming step showed a further drop in the enrichment ratio from 12 to 2.3. More detailed data are shown in Appendix Table 13.

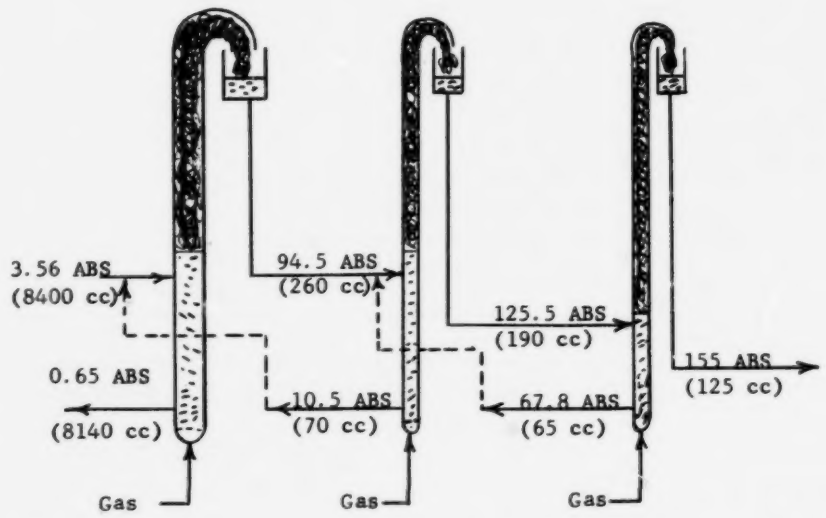
Run No.	Volume Of Liquid cc.	Foam Overhead cc.	Liquid Rejected As Foam	ppm ABS	Enrichment Ratio C_F/C_L
165A (Feed)	8,400	-	-	3.56	-
Product	8,140	260	3	0.65	145
166B (Feed)	260	-	-	94.5	-
Product	70	190	73	10.5	11.9
167B (Feed)	190	-	-	125.5	-
Product	65	125	66	67.8	2.3

(See Figure 8.)

Consecutive foaming stages, therefore, do not look feasible since the volume of the foam is reduced by a factor of two, and the product made is high in ABS.

An alternate scheme, however, would involve returning the residual liquid from the second column to the first column and introducing it with the fresh feed. The residual liquid from the third stage would also be returned to the second stage and mixed with the residual liquid from the first stage. This scheme is shown in Figure 8 by the dotted lines.

Figure 8



Refluxing Foam Overhead For Short Times May Increase COD Removal

It has been reported in the literature that refluxing the foam phase during foam fractionation runs enhances enrichment of the foam (5), although the effect of foam drainage is difficult to isolate from that of reflux (6). Therefore, exploratory runs were made to evaluate the effect of refluxing on the COD and ABS enrichment in the foam phase. The experimental data are summarized below, and more detailed results are given in the Appendix Table 14.

Reflux runs were made by returning all the collapsed foam phase to the foam fractionation column during the aeration period. At the end of the run, refluxing was stopped. The collapsed foam outside the column was not returned, and the liquid waste water remaining in the column was foamed until no more foam could be generated.

Run No.	Reflux Time, Min.	Foam Overhead, Vol. %	ppm COD	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.	-	-	104	4.2	-	-
69	15	5.4	42	0.23	59	94
70	30	5.7	81	0.34	22	92
71	60	5.2	92	0.31	12	93
Feed Sec. Eff.	-	-	102	5.45	-	-
196	0	1.6	101	0.49	1	91
197	15	0.5	99	0.40	3	92
198	15	0.7	50	0.40	17	92

Runs 69, 70 and 71 indicate that COD removal decreases from 59 to 12% as reflux time is increased from 15 to 60 minutes. Compared to some earlier runs, enrichments in the foam phase were better than with no refluxing. The decreased COD removals at longer residence times are due to higher final COD and ABS values since the foam overhead remains approximately constant for reflux times varying from 15 to 60 minutes. A possible explanation of these results is gradual air oxidation of the proteins and other water soluble organics in the waste water. Oxidation of these compounds to form polar hydroxyl groups, for example, would tend to decrease their surface activity, and hence, make their removal by foaming more difficult.

Runs 196, 197 and 198 were made to obtain a direct comparison of COD removal with and without refluxing on the same secondary effluent. COD removal is greater with refluxing but it does not affect ABS removal appreciably. The present refluxing procedure consisted of returning the collapsed foam liquid back to the foam column. This returned liquid ran down the glass walls of the column. Perhaps with the use of a liquid distributor, even greater advantages with refluxing can be obtained.

Effect Of Different
Gases On Removal By Foaming

A few batch foaming experiments were made using nitrogen, oxygen or ozone as the aeration gas. These experiments were made to determine if altering the gas would give greater removal of COD materials. It might be possible in some instances, by partial oxidation of the water soluble impurities, to increase their surface activity and hence increase their removal by foaming. Unfortunately, the data obtained show wide variation and it is not possible to obtain any firm conclusion on this point (Appendix Tables 15, 16, 17 and 18).

VI. FOAMING DISTILLED WATER CONTAINING VARIOUS SURFACTANTS

A brief study was made of foaming distilled water containing detergents, proteins and mixtures of the two. This study was initiated after it became evident that variation of the waste water effluent composition made the interpretation of the data in some cases very difficult. It was hoped that a better insight into foaming could be obtained from these experiments with relatively pure solutions and that ultimately a procedure could be found which would give complete COD removal from waste effluents by foaming. Many of the ideas explored here (pH, additives) were evaluated with waste water effluents and have already been described in this report, but some leads were not fully explored because of lack of time.

Effect Of pH On Foaming Solutions Of Synthetic Detergents

Foam fractionation runs were made to study the effect of pH on removal of detergents. Runs were made using dodecyl benzene sulfonate and sodium lauryl sulfate (both are anionic detergents) in distilled water. The solutions were foamed using a 2" diameter column and a fine gas disperser (nominal pore size 5 microns). More complete data are shown in Appendix Tables 19 and 20.

Run No.	pH	Detergent Additive	Foam Overhead Vol. %	ppm ABS	% Removal ABS	C_F/C_L
Feed - H_2O			-	14.2	-	
111	2.0	DBS*	8.9	0.78	95	194
110	2.4	"	3.9	1.08	92	312
109	6.6	"	9.1	6.50	54	14
107	11.5	"	16.1	2.13	85	36.3
108	11.9	"	13.9	1.03	93	93
Feed - H_2O			-	20.0	-	
116	2	SLS**	2.5	2.50	88	280
112	5.6	SLS	0.5	1.57	93	2,350
115	11.9	SLS	3.0	5.65	71	85.5

* Dodecyl benzene sulfonate (Solefonate) anionic.
** Sodium lauryl sulfate (Duponol) anionic.

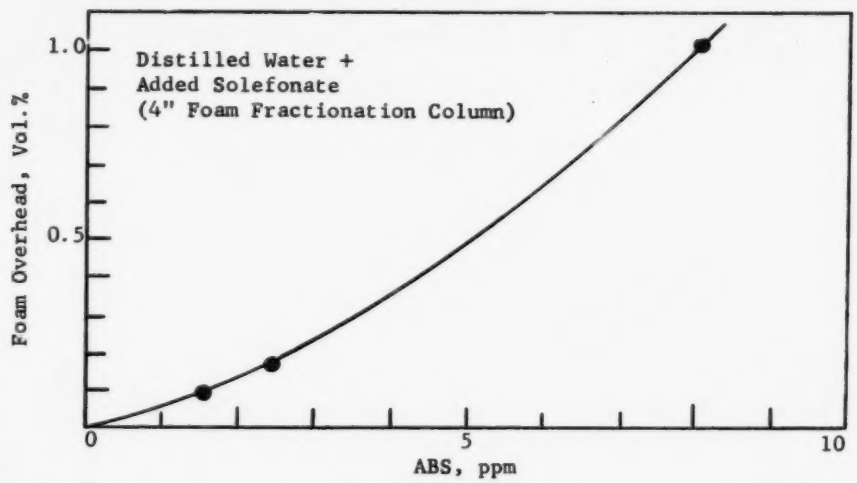
The data indicate that better removal was obtained with dodecyl benzene sulfonate, but this detergent had a higher volume of foam taken overhead. It was hoped that some general trend would be established between pH and the enrichment ratio but this was not possible. With the DBS, enrichments seemed to increase at pH values higher and lower than 7 while with the sodium lauryl sulfate, the reverse was true.

Foaming Solutions
Containing Low Concentrations Of ABS

Sometimes, the question arises as to the feasibility of removing very small concentrations of surfactants, in the order of 1-2 ppm. Foam fractionation was attempted on solutions containing ABS only in distilled water. The removal at the 1.5 to 2.5 ppm level in the feed was in the ragne of 20-35%. At 8 ppm of ABS in the feed, the removal was 74%.

The removal is low at the small concentration level because of the small amount of foam produced. Data showed that under the same conditions of gas rate, column diameter and residence time the amount foam produced increases with increase of ABS in the feed.

Figure 9



Data on the effect of ABS concentration on water surface tension and foam volume and stability are shown in Appendix Table 21 and Appendix Figure 1.

Better removal of ABS at very low concentrations can undoubtedly be obtained by using larger volumes of gas, longer residence time or possibly by the use of additives such as proteins. It will be shown later that very small concentrations of proteins interact with ABS to generate a large amount of foam.

pH Affects The Surface
Tension Of Proteins And Detergents

Surface tension measurements indicate that among the group of detergents studied at pH 7, the most surface active detergent was non-ionic (uncharged), followed by the cationic and anionic detergents. The protein, egg albumin, did not exhibit any surface activity at this pH.

At higher or lower pH values than 7, the surface tension of the protein, anionic and cationic detergents decreases. However, changing the pH had no effect on the surface activity of the uncharged detergent (see Appendix Figure 2).

	pH = 7		
Surfactant	Surface Tension Dynes/cm.	Foam Volume cc.	Foam Stability, Minutes
Tergitol (uncharged)	33.0	30	9.5
Ethoquad (cationic)	46.0	28	2.8
Duponol (anionic)	64.0	5	2
Protein	72.5	0	0

Foam volume and foam stability followed the same trends as the surface tension. Foam volume and stability were increased as the surface tension of the solution was decreased. Specifically, these two values were largest with the most surface active detergents, namely the non-ionics.

Variation of pH made it possible to create foam with proteins at values at higher and lower than 7. This makes it possible to remove the protein by foam fractionation. With the anionic detergent, more foam was created at pH higher and lower than 7. A reverese trend, less foam at pH higher and lower than 7 was observed with the uncharged and cationic detergent. More complete data on effect of pH on foam volume and foam stability of different detergents and the egg albumin are shown in Appendix Figures 3 and 4.

Ion pairs Offer Lead To Removal Of Weak Surfactants

Recent work reported in the literature (6) has indicated that it is possible to remove organic compounds which do not form stable foams themselves by foam fractionation. It was found that when the solute present in water was ionic, it could be removed by adding a surface active agent of the opposite charge. Thus, the enrichment ratios, $C_{Foam}/C_{Initial}$ in liquid for 1-naphthoic acid water solutions at pH of 9.5 (1-naphthoic acid negatively charged at these conditions) varied from 4.1 to 3.4 to 1.3 for added surfactants which were positively charged, uncharged and negatively charged, respectively. The enhanced separation is probably due to the formation of ion pairs between the solute and surfactant. In one case, spectral evidence has indicated clearly the formation of very stable ion pairs between a cationic surfactant and methyl orange. These results suggest that it may be possible to increase COD removal from secondary effluents by foam fractionation by using surfactants of different charges. The charged surfactants could form ion pairs with waste soluble organics of opposite charge, and both would be removed in the foam phase.

Proteins And Detergents Interact And Form More Foam Than Either One Alone Does

Data on foaming waste effluents has demonstrated that detergent removal is about 90-95% but COD removal is only 20-40%. It appears that a more fundamental study of foaming must be made to determine if COD removal can be improved. The experiments reported in this section were made to obtain a better understanding of protein-detergent interaction and the relative difficulty of their removal by foaming. Whether such data will help improve COD removal of actual waste waters is not known, but it may suggest new leads and guide future work.

Runs were made using distilled water which contained either added Solefonate (anionic detergent) or egg albumin or both. Batch foaming experiments were made using a 2" diameter column and a fine gas disperser. The data indicate that about twice as

Run No.	Additive, ppm		Foam Overhead, Vol. %
Feed-Distilled Water		None	0
95	38	Solefonate	7.5
96	38	Egg Albumin	0.02
97	38	Solefonate +	14.4
	38	Egg Albumin	

much overhead foam is generated when the detergent and protein are present together (run 97) than when the detergent is foamed alone (run 95). A negligible amount of foam is generated with the protein solution (run 96). More detailed data are shown in Appendix Table 22.

A possible explanation of the increased foam overhead with protein-detergent mixtures is that the protein shields the detergent molecules from one another and decreases the electrostatic repulsion between them. Detergent molecules contain a hydrophobic and hydrophilic part, these two are usually held together by an ionic or polar bond (R^+X^-), and the molecules are normally oriented vertically at the interface with the hydrophilic part in the water. This orientation of detergent molecules is similar to a row of vertical dipoles between which there exist strong electrostatic repulsion forces. Protein molecules, which may occupy spaces between such oriented detergent molecules, would decrease electrostatic repulsion and perhaps permit a higher final concentration of detergent at the interface, thus enhancing the foaming characteristics of the solution. Whether this hypothesis is generally true, or even applicable to actual waste water samples, is not certain. However, the results are interesting and suggest that small concentrations of proteins and detergents together be added to foamed effluents to generate more foam to increase COD removal.

Interaction Between Detergents And Protein Improve Separation By Foaming

The effect of altering pH on the removal of detergents and proteins from synthetic solutions was determined also. The data indicate a large foam overhead volume (10-20%) is collected at both high and low pH.

Run No.	Foam Overhead, Vol. %	pH	-----ppm------ COD	ABS	N	-% Removal- COD	ABS	N	C_F/C_L ABS	N	COD Due To Protein
Distilled water + additives*		-	58	9.40	7	-	-	-	-	-	-
154	13.5	2.0	15	0.54	5	74(64)	94	28	123	3.9	15
153	21.8	2.4	23	0.50	6	60(44)	95	14	83	1.7	4.8
152	11.2	11.5	34	0.91	8	41(18)	90	-	84	0	-
151	13.2	11.9	23	0.67	6	60(45)	93	14	100	2.3	7.1

* 38 ppm Solefonate, 38 ppm egg albumin.

Nos. in parentheses refer to COD removal due to proteins.
This is based on N values, total organic nitrogen analyses.

ABS removal is 90% or more at pH greater or less than 7. These results are similar to those obtained with secondary effluent. COD removal varies from 41 to 74%, but this includes ABS and proteins together. COD removal pertaining to proteins only varies from 18 to 64%. The latter figures were obtained by assuming 1 ppm ABS is equivalent to 2 ppm COD and substracting twice the ABS concentration from the COD content. Protein removal by total organic nitrogen analyses vary from 14 to 28%, but these values are believed to be less accurate than the previous estimation from COD analyses because the nitrogen values are very low. These data indicate that COD removal, the portion representing protein or egg albumin removal, is high at low and high pH levels and these results are similar to those obtained with secondary effluent. This supports the suggestion made previously that part of the increased COD removal occurs at low and high pH because protein removal is highest at these pH levels. More detailed data are shown in Appendix Table 23.

In the absence of Solefonate, egg albumin removal is low at all pH values.

Run No.	pH	Foam Overhead, Vol. %	ppm COD	% Removal COD	Enrichment Ratio, C_F/C_L COD
Feed[a]	-	-	58	-	-
144	1.9	10	31	46	9.7
143	2.2	10.5	43	26	4.3
147	6.8	0	62	-	-
145	11.5	0	58	0	1
146	12.0	3	58	0	1
148[b]	12.0	3.5	58	0	1
149[c]	12.0	4.8	55	5	2.1

a) 1000 cc. Distilled water, 40 cc. egg albumin soln., (1 cc. of soln. contains 1 ppm of additive), feed contains 0.04 ppm of egg albumin.
b) Foamed with N_2.
c) Foamed with O_2, all others foamed with air.

Maximum COD removal occurs at pH 2. Foam overhead volume increases at low and high pH levels, and this is in agreement with foam volume measurements reported in Appendix IV. The fact that egg albumin removal is considerably greater in the presence of Solefonate (compare runs 144 and 154) suggests strongly a specific interaction between the protein and detergent molecules such as ion-pair formation or simple electrostatic attraction perhaps. This specific interaction is probably more important for protein and detergent removal than the shielding effect of proteins suggested earlier. More detailed data are shown in Appendix Table 24.

These experiments with mixtures of egg albumin and Sclefonate indicate that interactions between them may lead to better removal of foaming than that obtained when either one is used alone. This suggests that small amounts of these surfactants be used as additives in future experiments with waste water effluents.

VII. CONTINUOUS FOAM FRACTIONATION

Continuous Foam Fractionation Experiments

Experiments were conducted where foam fractionation was carried out on a continuous basis in a 2" and 4" diameter column. In these studies, the variables studied were the gas rate in SCF/min., the residence time of the liquid in minutes, and the volume of the liquid in the foaming column.

Since several feeds were used, it was desirable to find one parameter by which all the data feeds can be correlated. This parameter was the ratio of concentration of ABS or COD in the residual liquid after steady state has been reached, C_{st}, to the concentration of ABS or COD in liquid feed to the foaming column, C_o. Therefore, high ratios C_{st}/C_o indicate poor removal, and low ratios indicate high removal.

Certain Minimum Gas Rates, And Residence Times Are Required For ABS Or COD Removal

At a residence time of 3 minutes and a 1000 cc. liquid volume in the foam column (column diameter 2") about 45×10^{-3} SCF/min. of air were required to decrease $C_{eqm.}/C_o$ below 0.2 for ABS and to 0.6 for COD. It appeared that below this rate the ABS and COD removal dropped drastically (see Figure 10).

At a gas flow rate of 63×10^{-3} SCF/min. and a 1000 cc. liquid volume in the foam column (column diameter 2") about 25 minutes of residence time were required to decrease $C_{eqm.}/C_o$ below 0.2 for ABS. Below this value, the ABS removal dropped drastically (see Figure 11).

The effect of varying the volume of waste water foamed on ABS and COD removal is shown in Figure 12. Constant air flow rate (108×10^{-3} SCF/min.) and residence time (3 min.) were used in these experiments. The data indicate that ABS removal decreases as the volume of liquid foamed is increased. This behavior is expected because the total gas used to waste water volume ratio is greatest at the low liquid volumes. COD removal did not change during these runs. However, these experiments indicate only general trends and more work is required with the continuous foam fractionation unit.

Figure 10

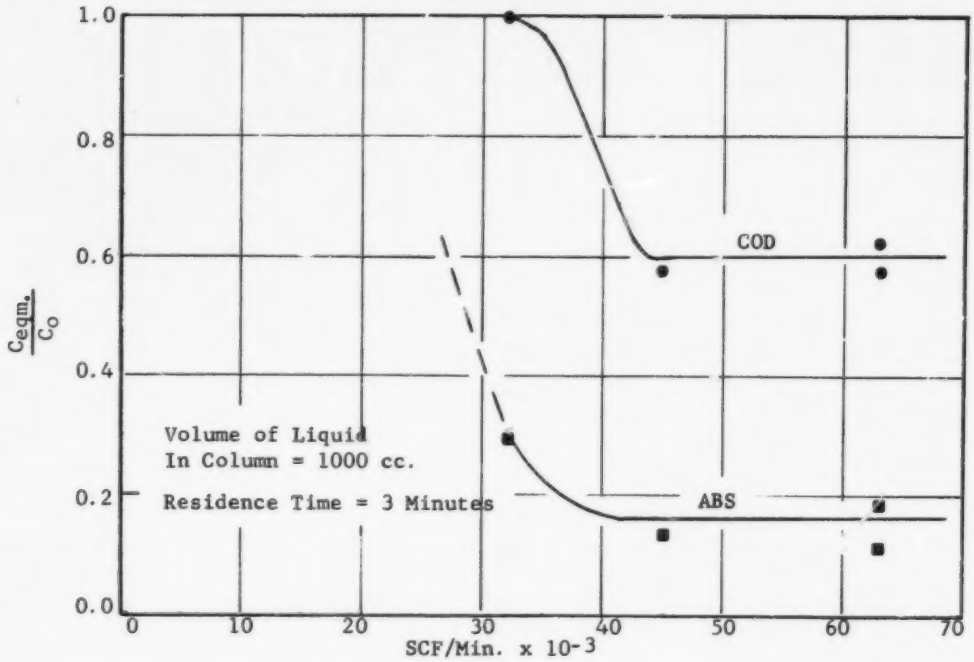


Figure 11

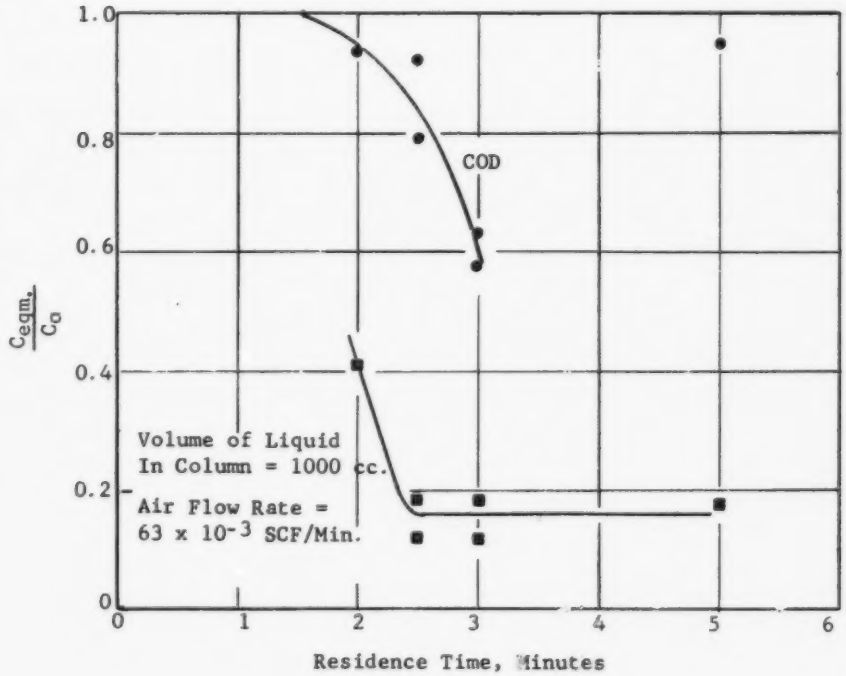
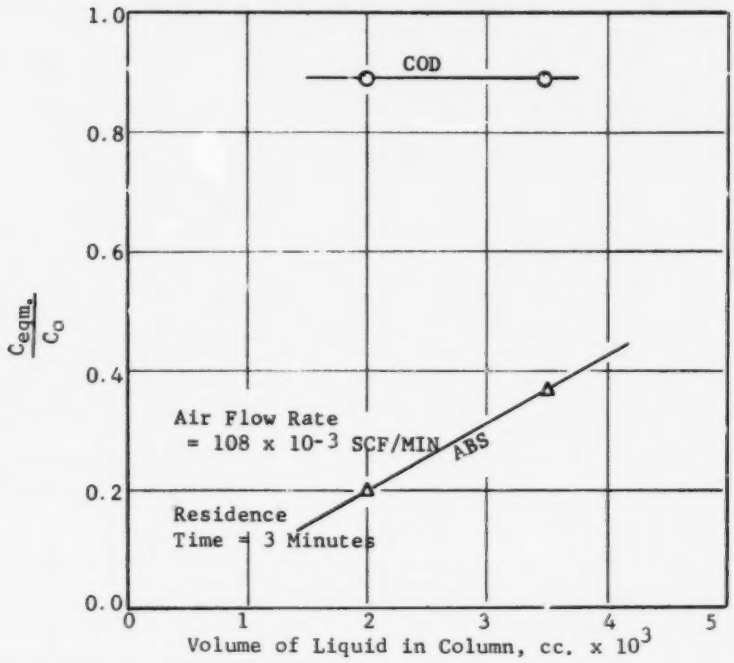


Figure 12



Ratio Of Volume Of
Gas/Volume Of Liquid Provides
General Correlation For Continuous Data

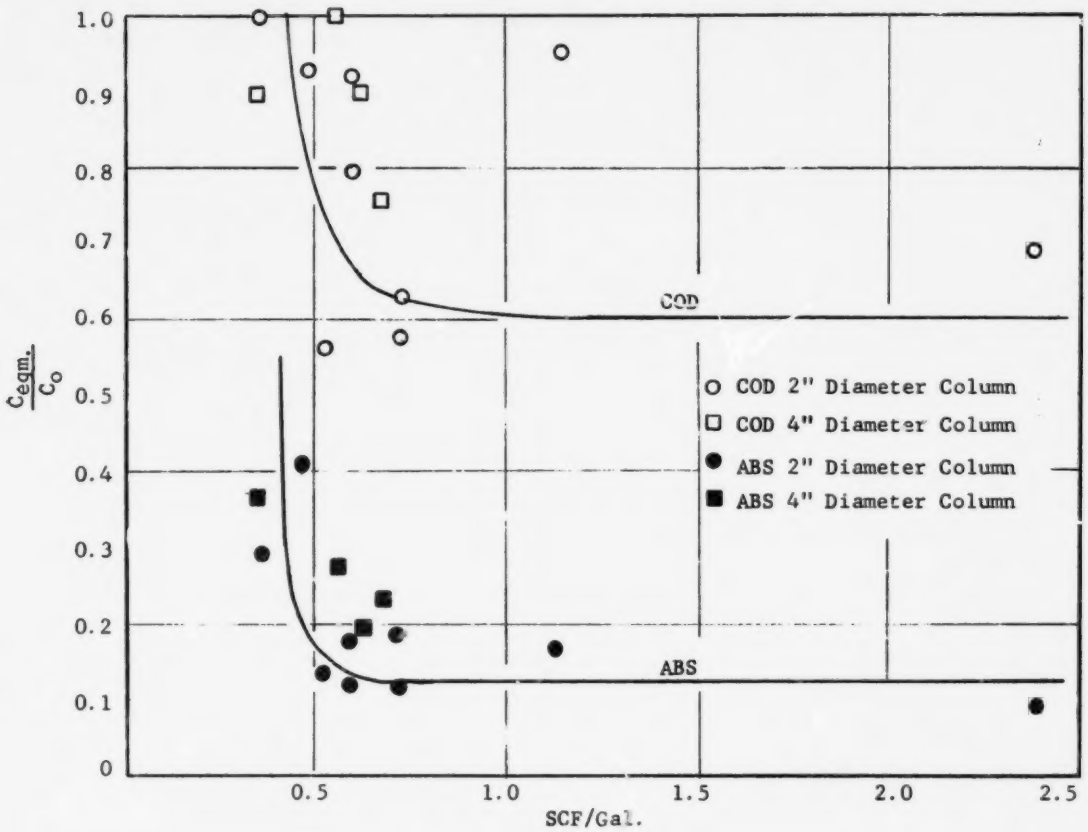
So far the effects of gas rate, residence time, and reactor volume have been discussed as variables affecting the separation by foam fractionation. These three variables can be combined as:

$$\frac{\text{SCF Gas}}{\text{Min.}} \times \text{Residence Time, Min.} \times \frac{1}{\text{Liquid Volume, Gal.}}$$

to give a quantity which is the SCF of gas/gal. of liquid treated. This quantity seems to correlate all of the data.

It appears that a certain minimum value of SCF of gas per gallon of liquid is required. The quantity is about 0.8. Below this value, both ABS and COD removal drops drastically (see Figure 13). A summary of the results from the continuous foam fractionation runs is shown in Appendix Table 25. More detailed data are shown in Appendix Table 26.

Figure 13



In summary, studies on foam fractionation in the continuous unit show ABS can be removed in such equipment. Effective separations require at least 0.8 SCF of air per gallon of waste effluent. A liquid residence time of no less than 2.5 minutes and no more than 4 seems adequate for reducing ABS content from 2-7 ppm down to 0.5 ppm.

Analysis Of The Foam
Fractionation Operation As A Dynamic System

Understanding the mechanism by which the foaming process works provides a guide by which it is possible to adjust the operating variables (e.g., feed rate, gas rate, etc.) such that a satisfactory product can be made.

For example, the foam fractionation plant may be able to reduce the ABS concentration of a 2 ppm feed down to 0.5 ppm with a residence time of 2 minutes. An increase in ABS concentration of waste water may occur early in the morning, 7:00 AM. If the residence time is unchanged, the effluent from the plant may now contain 2.5 ppm, while the product specifications is 0.5 ppm. If a control system designed to respond to the increases in feed concentration by reducing the feed rate is built in the system, it will be possible to make a satisfactory product of 0.5 ppm ABS from a 5 ppm ABS feed.

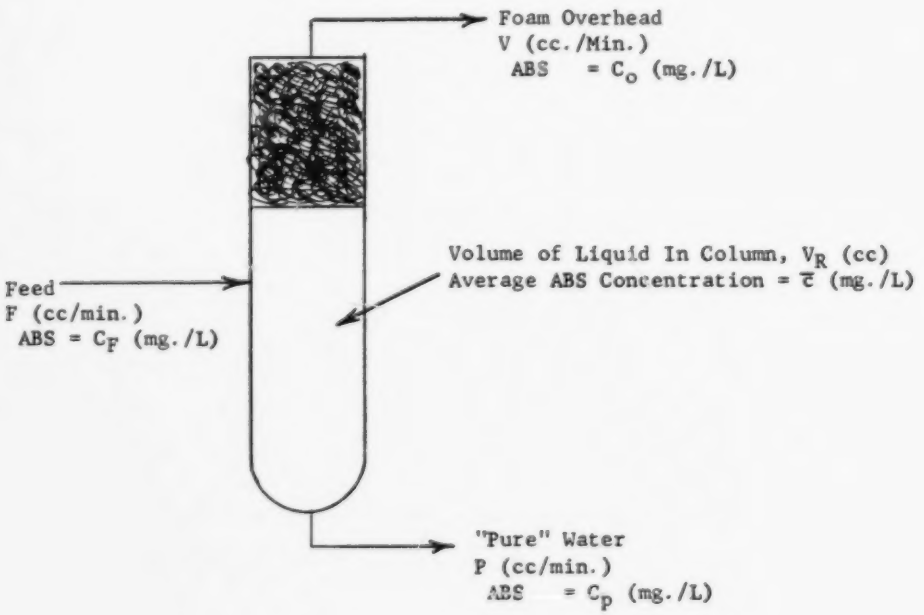
In order to design a control system, the relation between the feed to product concentration with the operations variables must be established. The simplest form of relationship is that expressing the disappearance of the ABS as a function of initial concentration, residence time and some constant k which is characteristic of this type of process. This constant may be similar to the rate constant in chemical reactions.

The mathematics of treating chemical conversions in continuous reactors (8) have been used here to predict the time during which steady state or equilibrium is approached, also the level of the final concentration in the effluent after time, t. Models describing approaches to relate the initial final concentrations with time and reaction constant are discussed in the following section.

Model I

The change of ABS concentration with time of waste water foamed in a continuous unit can be obtained from the apparatus shown in Figure 14. In order to understand this method of analysis, variables must be defined and certain assumptions must be made.

Figure 14



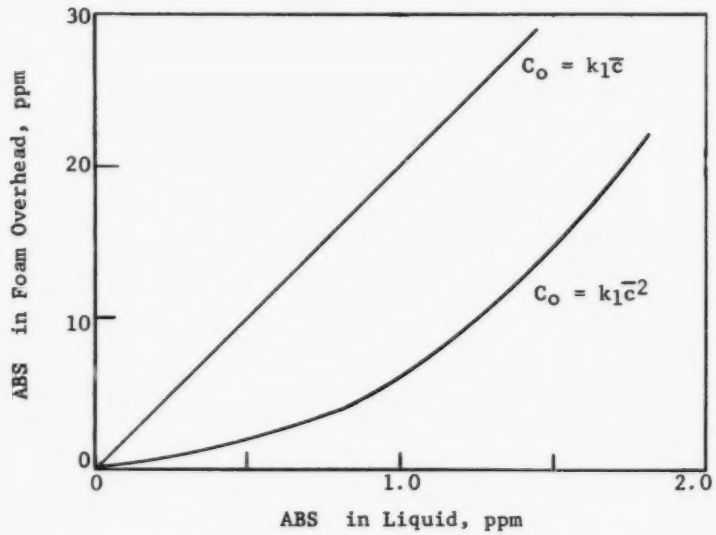
Assumptions

The object is to calculate how the average ABS concentration, $\overline{c}$, changes with time in the column. The assumptions are made that the foam fractionation column is operated so that the feed inlet, F, the foam overhead, V, and the "pure" water outlet, P, flow rates are kept constant during a run. Also, the volume of waste water in the column, V_R, is kept constant, and the ABS concentration in the feed inlet and "pure" water outlet are constant during a run. A further assumption is made that the concentration of ABS in the foam overhead is proportional to the n^{th} power of the average ABS concentration in the column.

$$C_o = k\ (\overline{c})^n \qquad (1)$$

The constant k depends on column geometry and other operating conditions. The two cases for n=1 and n=2 are treated in this analysis. It should be possible to determine the relationship between C_o and $\overline{c}$ by foaming effluents of varying ABS concentration and analyzing the foam overhead. A plot of C_o versus $\overline{c}$ would then permit an experimentally determined value of n to be chosen. It is possible, of course, that some relationship other than equation (1) may give a better representation of the experimental data (see Figure 15).

Figure 15



Material Balance

A material balance is made for ABS in the foam fractionation unit for a small interval of time, dt minutes.

$$\text{Input} = \text{Accumulation} + \text{Output} \tag{2}$$

$$F \frac{(cc.)}{(min.)} dt\ (min.)\ C_F \frac{(mg)}{(L)}\ 10^{-3} \frac{(L)}{(cc.)} = V_R\ (cc.)\ d\bar{c} \frac{(mg)}{(L)}\ 10^{-3} \frac{(L)}{(cc.)}$$

$$+ V \frac{(cc.)}{(min.)} dt\ (min.)\ C_o \frac{(mg)}{(L)}\ 10^{-3} \frac{(L)}{(cc.)} + P \frac{(cc.)}{(min.)} dt\ (min.)\ C_p \frac{(mg)}{(L)}\ 10^{-3} \frac{(L)}{(cc.)} \tag{3}$$

$$FC_F\, dt = V_R d\bar{c} + VC_o\, dt + PC_p dt \tag{4}$$

Rearranging,

$$\frac{-d\bar{c}}{dt} = \frac{VC_o}{V_R} + \frac{PC_p}{V_R} - \frac{FC_F}{V_R} \tag{5}$$

Or,

$$-\frac{d\bar{c}}{dt} = k\bar{c}^n + B \tag{6}$$

where

		Units
$B = p - f$		(mg/L/min.)
$k = \frac{V}{V_R} k_1$		($min.^{-1}$)
$p = \frac{Pc_p}{V_R}$		(mg/L/min.)
$f = \frac{FC_F}{V_R}$		(mg/L/min.)
$C_o = k\ (\bar{c})^n$	n, k are constants, no units	

For n = 1, equation (6) becomes

$$-\frac{d\bar{c}}{dt} = k\bar{c} + B \tag{7}$$

Therefore,

$$-\frac{1}{k}\ln(k\bar{C}+B) = t + \text{constant} \tag{8}$$

Initial Conditions: $\bar{C} = \bar{C}_o$, $t = 0$

Therefore,

$$\frac{1}{k}\ln\frac{(k\bar{C}_o + B)}{(k\bar{C} + B)} \tag{9}$$

or

$$\bar{C} = \frac{B}{k}(e^{-kt}-1) + \bar{C}_o e^{-kt} \tag{10}$$

For n = 2, equation (6) becomes

$$-\frac{d\bar{C}}{dt} = k\bar{C}^2 + B \tag{11}$$

And using integration formulas (a),

$$\int\frac{dx}{ax^2+c} = \frac{1}{2\sqrt{ac}}\ln\left(\frac{x\sqrt{a}-\sqrt{-c}}{x\sqrt{a}-\sqrt{-c}}\right) \tag{12}$$

where

$a<0,\ C>0$

$$\int\frac{dx}{ax^2+c} = \frac{1}{2\sqrt{-ac}}\ln\left[\frac{\sqrt{c}+x\sqrt{-a}}{\sqrt{C}-x\sqrt{-a}}\right] \tag{13}$$

where

$a<0,\ C>0$

$$\int\frac{dx}{ax^2+c} = \frac{1}{\sqrt{ac}}\tan^{-1}\left(x\sqrt{\frac{a}{c}}\right) \tag{14}$$

where

$a>0,\ c<0$

Initial Conditions: $t = 0,\ \bar{c} = \bar{C}_o$

We get:

$$t = \frac{1}{2\sqrt{-kB}} \ln \left[\frac{(\bar{C}_o\sqrt{k} - \sqrt{-B})}{(\bar{C}_o\sqrt{k} + \sqrt{-B})} \frac{c\sqrt{k} + \sqrt{-B})}{(\bar{c}\sqrt{k} - \sqrt{-B})} \right] \tag{15}$$

where

$k>o,\ B<0$

$$t = \frac{1}{2\sqrt{-kB}} \ln \left[\frac{(\sqrt{B} + \bar{C}_o\sqrt{-k})}{(\sqrt{B} - \bar{C}_o\sqrt{-k})} \frac{(\sqrt{B} - \bar{C}\sqrt{-k})}{(\sqrt{B} + \bar{C}\sqrt{-k})} \right] \tag{16}$$

where

$k<0,\ B>0$

$$t = \frac{1}{\sqrt{kB}} \tan^{-1}\left(\bar{C}_o\sqrt{\frac{k}{B}}\right) - \frac{1}{\sqrt{kB}} \tan^{-1}\left(\bar{c}\sqrt{\frac{k}{B}}\right) \tag{17}$$

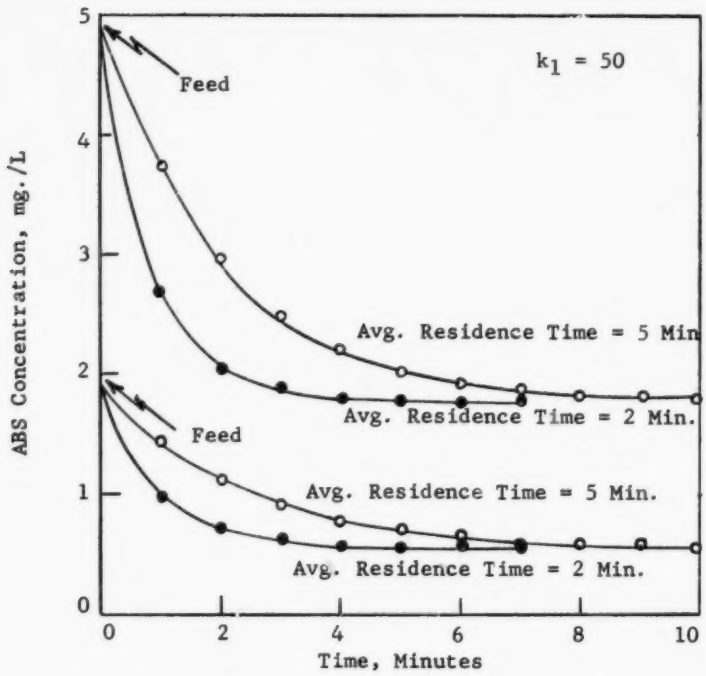
where

$k>0,\ B>0$

(a) Handbook of Mathematical Tables and Formulas, R. S. Burington, Handbook Publishers, Inc., Sandusky, Ohio (Pg. 64).

The case for n=1 has been used to calculate the average ABS concentration, $\bar{c}$, at residence times of 2 and 5 minutes, initial ABS concentrations, $\bar{C}_o$, of 2 and 5 mg/L, and for k_1 values of 10 and 50. In these calculations the column volume, V_R is 1000 cc. and the foam overhead is assumed to be 5 vol. %. The ABS concentration in the "pure" water outlet is taken as 0.5 mg/L. The calculations are summarized in Appendix Table 27 and plotted below (see Figure 16).

Figure 16



This model allows several conclusions to be made about the foaming process in a continuous unit. These are listed below.

- For k_1 values of 10 the model predicts an increase in ABS concentration in the column with time. For k_1 equal to 50 the ABS concentration decreases with time. These results indicate that the magnitude of k_1 is an important factor which determines how rapidly ABS is removed from waste water. In practice ABS will never increase in the liquid in the column; and, therefore, this analysis of foaming does not represent any real situation when k_1 has low values.

- The ABS concentration, $\bar{c}$, versus time curves indicate that at the chosen conditions of 5 vol. % foam overhead and k_1 = 50, the ABS concentration is decreased from 2 to 0.6 mg/L and from 5 to 1.8 mg/L. A lower ABS content for the 5 mg/L case was not obtained probably because of the particular values chosen for foam overhead and k_1. The important point is that the model demonstrates that lower final ABS content is obtained with waste water containing 2 mg/L of ABS. The model overestimates the difference between foaming 2 and 5 mg/L of ABS solutions. In practice, foaming 5 to 2 mg/L ABS solutions removes about 95% of the ABS (0.70 to 0.10 mg/L ABS is the final concentration).

- No calculations were made for the case n=2 because improvements were introduced for n=1 and these are presented in Model II.

Model II

The objective here is to calculate how the average ABS concentration, $\bar{c}$, changes with time in the foam fractionation column. The quantities used here have the same meaning as described in Model I. The main difference between Models I and II is that some basic assumptions are changed.

Assumptions

The same assumptions are made here as in Model I except that the ABS concentration of the "pure" water outlet, C_p, is not kept constant, but it is assumed that C_p is the same as the average ABS concentration in the column, $\bar{c}$. This assumption is perhaps more realistic then that made in Model I because C_p must vary with time during the initial stages of a foam fractionation run. C_p must vary from C_F to some minimum value which depends on the operating conditions. However, even this assumption that the "pure" water outlet ABS concentration is $\bar{c}$ is a great simplification of the real physical situation in the column; there is probably a concentration gradient of ABS and other impurities in the column.

Material Balance

A material balance is made for ABS in the continuous unit as before.

$$\text{Input} = \text{Accumulation} + \text{Output} \tag{1}$$

$$Fc_F dt = V_R d\bar{c} + Vc_o dt + P\bar{c}dt \tag{2}$$

Rearranging,

$$-\frac{d\bar{c}}{dt} = \frac{Vc_o}{V_R} + \frac{P}{V_R}\ \bar{c} - \frac{FC_F}{V_R} \tag{3}$$

and using

$$C_o = k_1 \bar{c}^n \tag{4}$$

$$-\frac{d\bar{c}}{dt} = \frac{V}{V_R}\ k_1\ \bar{c}^n + D\ \bar{c} - f \tag{5}$$

or

$$\frac{d\bar{c}}{dt} + D\bar{c} - f = -kc^{-n} \tag{6}$$

where

	Units
$D = \frac{P}{V_R}$	(Min.$^{-1}$)
$k = \frac{V}{V_R}\ k_1$	(Min.$^{-1}$)
$f = \frac{FC_F}{V_R}$	(mg/L/min.)

n, k_1 are constants, no units

For n = 1, equation (6) becomes

$$-\frac{d\bar{c}}{dt} = \bar{c}\ (D+K)^{-f} \tag{7}$$

Equation (7) is similar to equation (7) of Model I except for different constants.

Therefore,

$$-\frac{1}{(D+K)}\left[\ln\ \bar{c}(D+k) - f\right] = t + \text{Constant} \tag{8}$$

Initial Conditions: $\bar{c} = \bar{C}_o$, t = o

Therefore,

$$\frac{1}{(D+k)}\ln\left[\frac{C_o\ (D+k) - f}{\bar{c}\ (D+k) - f}\right] = t \tag{9}$$

or,

$$\bar{c} = \frac{f}{D+k}\ (1-e^{-(D+k)t}) + \bar{c}_o e^{-(D+k)t} \tag{10}$$

For n = 2, equation (6) becomes

$$-\frac{d\bar{c}}{dt} = k\bar{c}^2 + D\bar{c} - f \tag{11}$$

$$-\int \frac{d\bar{c}}{k\bar{c}^2 + D\bar{c} - f} = \int dt \qquad (12)$$

And using the integration formula (1),

$$\int \frac{dx}{a + bx + cx^2} = \frac{1}{\sqrt{b^2 - 4ac}} \ln \left[\frac{2c\,x + b - \sqrt{b^2 - 4ac}}{2c\,x + b + \sqrt{b^2 - 4ac}} \right]$$

where

$$b^2 > 4ac$$

Initial Conditions: $t=0$, $\bar{c}=\bar{C}_o$

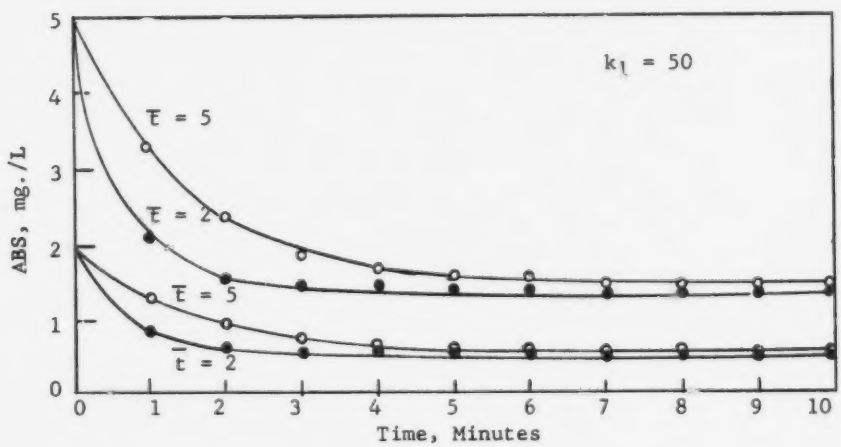
We get:

$$(2k\bar{C}_o + D + \sqrt{D^2 + 4fk})\,(2k\bar{c} + D - \sqrt{D^2 + 4fk}) =$$

$$(2k\bar{C}_o + D - \sqrt{D^2 + 4fk})\,(2k\bar{c} + D + \sqrt{D^2 + 4fk})\, e^{-\sqrt{D^2+4fk}\;t}$$

The case for n=1 has been used to calculate the average ABS concentration, $\bar{c}$, at residence times of 2 and 5 minutes, initial ABS concentrations, $\bar{c}_o$, of 2 and 5 mg/L and for k_1 values of 10 and 50. The column volume V_R, is 1000 cc. and the foam overhead is assumed to be 5 vol. %. The calculations are summarized in Appendix Table 28 and plotted below (see Figure 17).

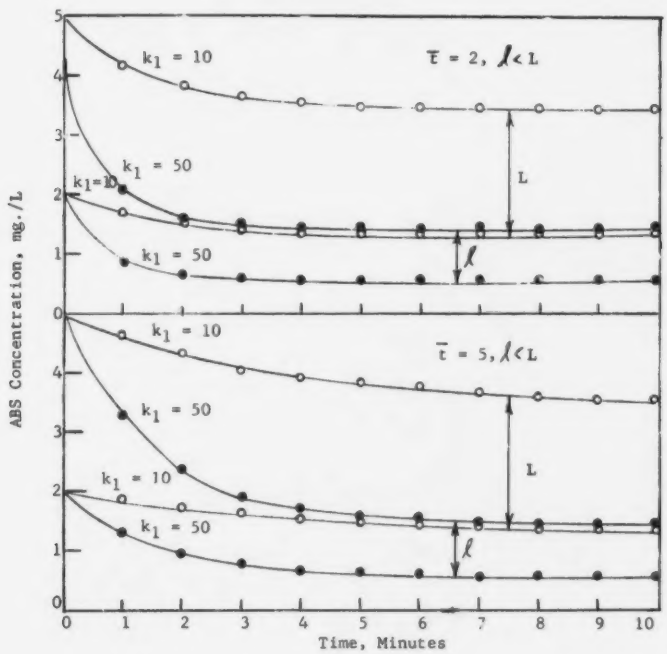
Figure 17



The conclusions which can be made about the foaming process from this model are listed below.

- This model predicts that ABS concentration decreases with time for k_1 values of 10 or 50. This is an improvement over the first model.
- For k_1 = 50, lower final values of ABS are obtained for 2 mg/L than for 5 mg/L solutions. This is in agreement with the first model and with experimental results in general.
- This model predicts that ABS concentration decreases more rapidly for a residence time of 2 minutes than for 5 minutes. This does not appear to be reasonable on the basis of experimental work. A longer residence time generally means more ABS will be removed by foaming and the final ABS concentration will be lower. It is possible that too many restrictions have been used in this model and a more detailed treatment is needed to describe the residence time effect in foaming. For example, the foam overhead volume probably depends on the ABS concentration and this could be taken into account in a more detailed analysis, or it may be accounted for in this treatment as will be shown later.
- The effect of altering k_1 is shown below. For k_1 = 50, the difference between the final ABS concentrations from feeds of 2 and 5 (mg/L), 1, is smaller than L, the difference between the final ABS concentrations from feeds of 2 and 5 mg/L with a k_1 = 10 (see Figure 18).

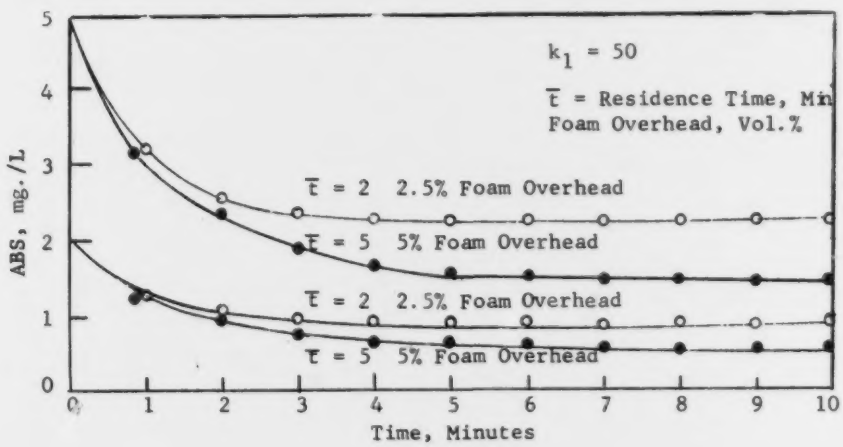
Figure 18



Experimentally, it has been observed that foaming 2 or 5 mg/L of ABS solutions gives 95% ABS removal and the final ABS content is practically the same (0.7 - 0.1 mg/L of ABS). Therefore, the model gives a better representation of the data with a k_1 value of 50 than with 10. Some experimental values of k_1 are shown in Appendix Table 29. The k_1 values can vary from 5 to 163 for ABS removal. These k values were calculated to equal C_f/C_{Feed} or $k_1 = C_o/\bar{\tau}$, the nomenclature used in this mathematical development using n = 1, see equation (1) page 49.

The effect of altering foam overhead volume and residence time on ABS concentration in the column is shown below (see Figure 19). In general, if aeration

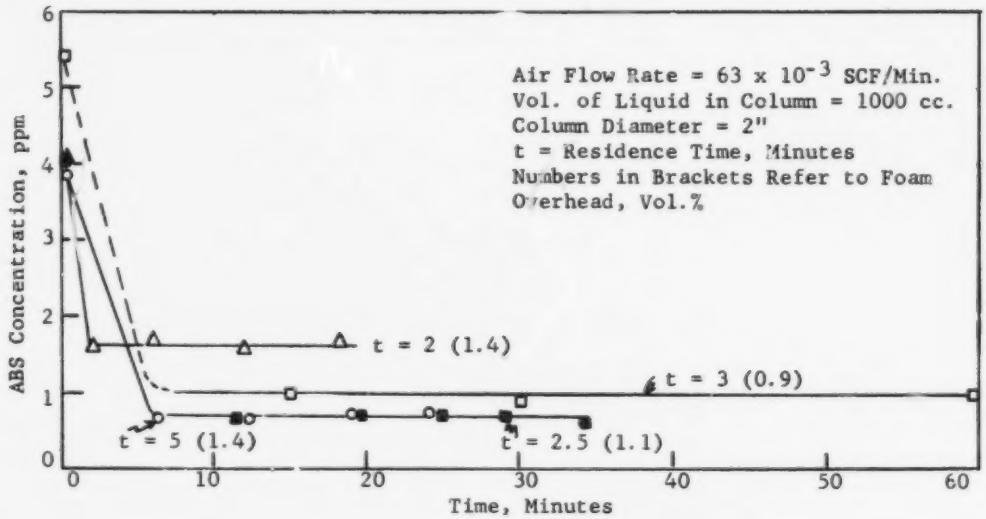
Figure 19



and other conditions are kept constant, then more foam overhead is collected as residence time is increased (e.g., 2 to 5 minutes). If this fact is taken into account in the calculation, the model predicts that under these conditions more ABS will be removed at the longer residence time and this is in agreement with experiment.

Some typical experimental ABS concentration versus time curves for continuous runs in 2" columns are shown below (see Figure 20). The data indicate that for an

Figure 20



initial ABS concentration of 4 ppm, residence times of 5 to 2.5 minutes are sufficient to lower the ABS concentration to about 0.6 - 0.7 ppm, but a residence time of 2 minutes lowers the ABS from 4 to only 1.6 ppm. This behavior is similar to that predicted by Model II. These data empahsize that if the residence time is sufficiently long to give high ABS removal for a given waste water feed, it may not necessarily give high ABS removal when the initial ABS concentration in the waste water feed is increased. This case is shown above for a residence time of 3 minutes and an initial ABS concentration of 5.4 ppm. After foaming the ABS concentration is lowered to only 1 ppm.

How Does Mathematical
Model Of Foaming Operation
Help In Practical Situations

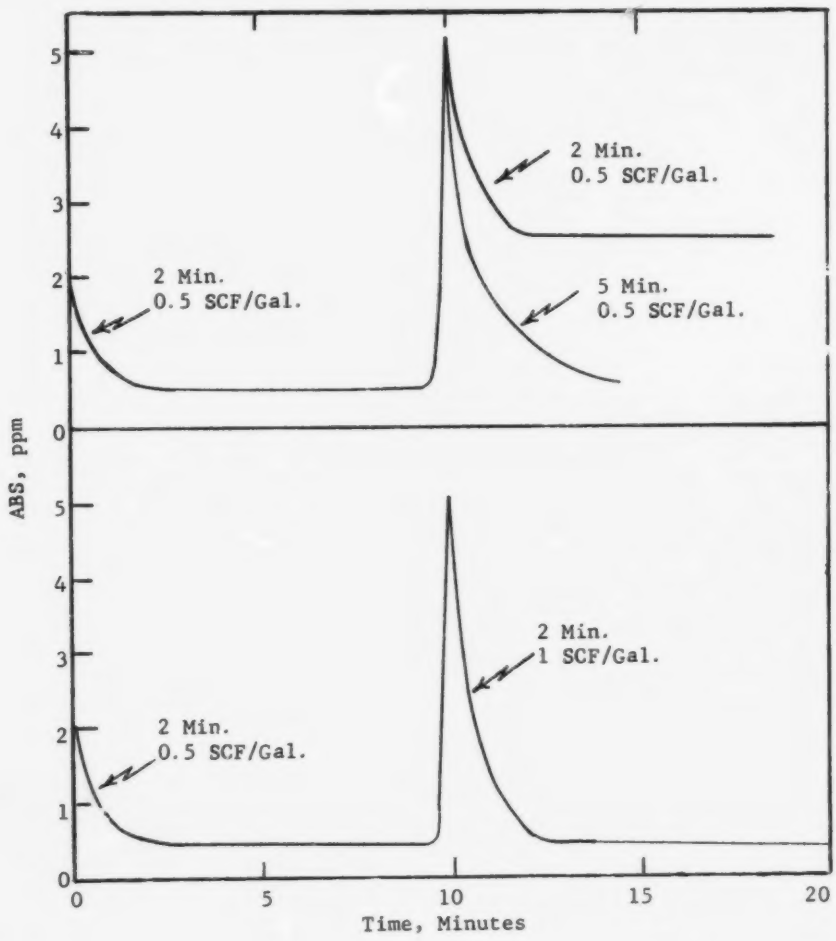
At a residence time of 2 minutes and a gas rate of 0.5 SCF/gal. it may be possible to reduce the ABS content of a waste effluent from 2 to 0.5 ppm. If however, the ABS content rises suddenly to 5 ppm such as in the early hours of the morning, using these same conditions it will never be possible to make a specification product of 0.5 ppm ABS.

There may be some ways to make a 0.5 ppm ABS product from a 5 ppm ABS feed, this could be by maintaining the same gas rate, but increasing the residence time from 2 to 5 minutes. Increasing the residence time may not always be practical such as in hours where the flow to the waste plant is high in both volume and ABS content. To handle this situation, it would then be desirable to keep the residence time low (2 minutes) but increase the gas rate from 0.5 to 1 SCF/gal.

One of the best ways to be able to handle these changes in feed concentration is to establish the factors which affect separation by foaming. Using these physical properties, it will then be possible to install automatic control systems that will respond properly to changes in the nature of the feed.

This approach constitutes a very challenging study and perhaps provides the greatest contribution to the proper commercialization of the foam fractionation operation (see Figure 21).

Figure 21



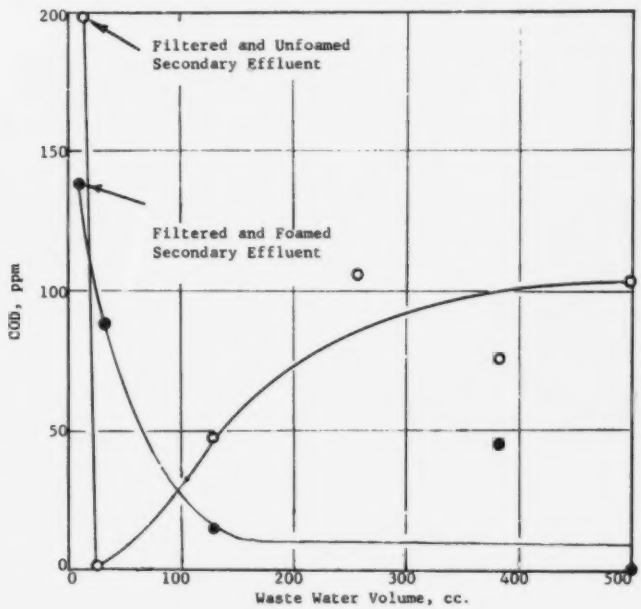
VIII. FOAMING IN COMBINATION WITH ADSORPTION

Adsorption Preceded By Foaming Can Give Low COD

Several different approaches such as use of additives and variation of pH have been described so far for obtaining maximum COD removal. An alternative approach is that of using a carbon adsorption step after the waste effluent has been foamed. Foaming removes the high molecular weight very surface active materials such as the ABS, and some proteins. These materials have sufficiently large molecules that they can plug the pores of the carbon adsorbent and reduce its capacity. Therefore, adsorption runs using foamed and unfoamed secondary waste effluent were made to evaluate this approach.

Initial runs were made using 1.6 gms. (5 cc.) of activated carbon (surface area* = 1408 $m^2/gm.$) in a glass burrette which made an adsorption bed about 2.5 inches long. The waste water effluent was collected in 25 cc. volumes, and COD analyses were obtained on several fractions in each run. The runs were terminated when 100 volumes of waste water effluent had passed over 1 volume of activated carbon. The results indicated that a water product of low COD content can be made if the waste effluent has been prefoamed. With waste water which has not been prefoamed, a zero COD product was made only in the first 5 volumes of liquid passed over the bed. The COD in the product then rose very quickly. On the other hand with the prefoamed effluent, 100 volumes of waste water were passed over the bed, and COD content of the product was still low. More detailed data are shown in Appendix Table 30 (see Figure 22).

Figure 22

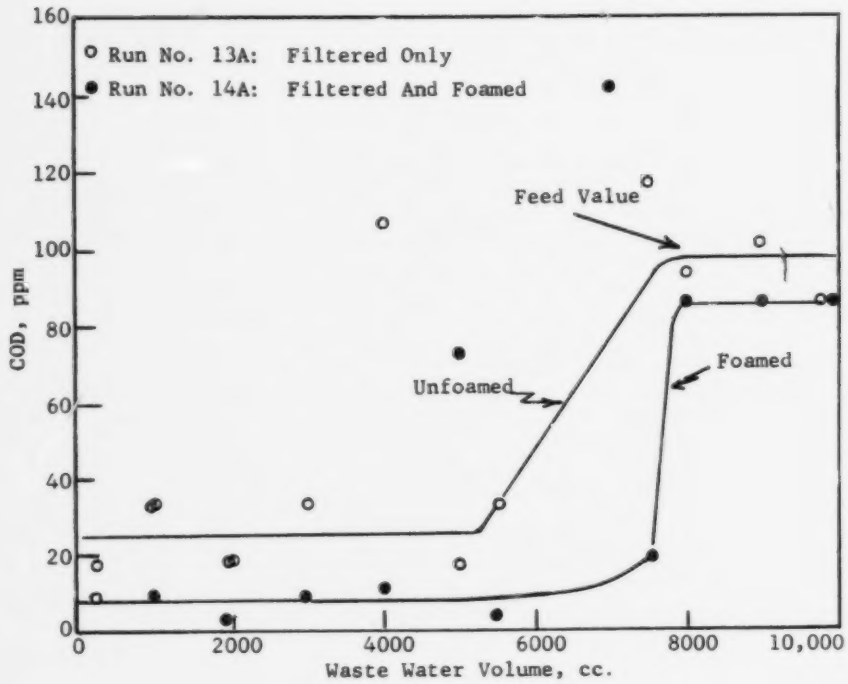


* Determined by N_2 adsorption and BET theory.

Preceding page blank

Following these earlier experiments, larger scale runs using 100 rather than 5 cc. of carbon were made. The adsorption bed was cylindrical and was about 6" deep, and 1" in diameter. Both foamed and unfoamed secondary waste water effluents were used for comparison purposes as described earlier (see Figure 23).

Figure 23



The data confirmed the earlier findings. Foaming and adsorption made a product of lower COD, than adsorption alone 10 vs. about 25 ppm of COD. The adsorption step decreased COD from 80 ppm to an average of 20 ppm during the initial stage of the adsorption run, which represents 49% COD removal. The combination of foaming and activated carbon adsorption removed 76% of the COD material. More detailed data are shown in Appendix Table 31.

Several more experiments were made by passing foamed and unfoamed secondary effluents over activated carbon. The data are presented in Appendix Figures 5 and 6 and Appendix Tables 32, 33 and 34. All the data tend to support the general conclusion that activated carbon has higher adsorption capacities with foamed than with unfoamed effluents. However, the activated carbon capacities vary depending on the sample of waste water that is used. It is entirely possible that the advantage of foaming waste water prior to treatment with activated carbon may be negligible in some instances.

IX. EMULSION FRACTIONATION

Emulsion Stability Of Secondary Effluent With Organic Solvents Determined

The first phase for evaluation of emulsion fractionation requires determination of the emulsion stability. If the stability is poor, the surfactants concentrated at the interface will return to either the aqueous or organic phase in whichever they are more soluble.

Emulsion stabilities of secondary effluent with organic solvents were determined. These measurements were made by shaking by hand 25 cc. of secondary effluent, or the effluent diluted in distilled water with 25 cc. of the organic solvent, for 30 seconds in a 100 cc. graduated cylinder at a uniform rate (about 4 feet/sec.). Emulsion stabilities were expressed in terms of the time required for the emulsion phase to collapse.

The solvents screened were chosen to represent the four general types of hydrocarbons - paraffins (n-heptane), olefins (hexane-1), aromatics benzene and (toluene) and cycloparaffins (decahydronaphthalene). Also, nitrobenzene (μ = 4.2 debyes) was used to determine the emulsion stability with a highly polar solvent. The data indicate that the solvents can be divided qualitatively into two groups. One group of solvents, nitrobenzene and hexene-1, exhibit decreasing emulsion stabilities with dilution of the secondary effluent. The second group of solvents, decahydronaphthalene, benzene, toluene and n-heptane, exhibit increasing emulsion stabilities with dilution of the secondary effluent. The precise reason for this difference in behavior is unknown now. But, possibly the polar nature of a solvent may be an important factor in determining the emulsion stability of solvent-water mixtures. See Appendix Table 35 for complete data.

So Far Emulsion Fractionation Does Not Look Promising For Removal Of Soluble Organics

A mixture of 200 cc. of secondary effluent was shaken with 200 cc. of solvent for 30 seconds. The emulsion layer was allowed to form and a sample of the waste water was taken for COD analysis. The waste water sample was then filtered through Whatman #5 filter paper to remove any trace amounts of solvent. None of

Solvent, cc.	Emulsion Stability Seconds	Product, COD, ppm
Nil		157 (Feed)
n-Heptane	15	146
Toluene	50	345
Decahydronaphthalene	120	260
Benzene	-	453
Hexene	10	1,785
Nitrobenzene	35	948

the solvents seem to give any appreciable reduction of COD. The increase in COD content is probably due to the dispersion or solution of trace amounts of the organic liquid in the water. Paper filtration did not remove the trace amounts of suspended organic liquid. It is conceivable that centrifugation will.

Over-all, however, compared to foam fractionation, emulsion fractionation does not look promising. See Appendix Figure 7 for an illustration of a laboratory scale continuous emulsion fractionation unit. It may be possible to use this unit to obtain COD and ABS removal using emulsion fractionation. This unit was not built and it is not known if such a unit has been proposed or used by other workers.

X. ECONOMICS OF FOAM FRACTIONATION PROCESS

The economics of the foam fractionation process were worked out by estimating the investment costs and the operating costs.

Cases Studied

Five cases were studied, these were in gallons/day; 108×10^3, 1.08×10^6, 10.8×10^6, 54×10^6, 108×10^6. The low capacity evaluations were designed to handle small industrial waste systems where foam fractionation can be applied. The larger capacity evaluations were designed to handle effluents from sewage treatment plants.

Process Basis Specifications

The two most important process variables fixed were the gas rate in terms of standard cubic feet per gallon, and the residence time in minutes for the water in the foam column. Based on the experimental results from the continuous runs a gas rate of 0.8 SCF/gal. of water was chosen. It can be seen from Figure 13 that gas rates above this value do not improve ABS or COD removal. At this gas rate the residence time was 3 minutes. Here again, it can be seen from Figure 11 that residence times beyond 3 minutes do not appear to improve ABS removal. The effect of residence time on COD removal is not clear from Figure 21. The target product contains 0.5 ppm ABS or less. The feed generally contains 2-7 ppm ABS.

Once the water capacity and residence time are determined, it is possible to calculate the pump type and horsepower. After the water capacity and gas rate in SCF/gal. (0.8 here) have been fixed, it is possible to calculate the compressor type and horsepower.

Since compression will raise the temperature of the air up to as much as 230°F., it is necessary to cool the air down to ambient conditions. To do that, the compressors should be equipped with water coolers. From a knowledge of the compressor inlet and outlet pressures it is possible to calculate the exit-air temperature. The heat load to be removed in BTU/day is then calculated from a knowledge of the rise in temperature, the pounds of air per day and the specific heat of air.

Equipment Design

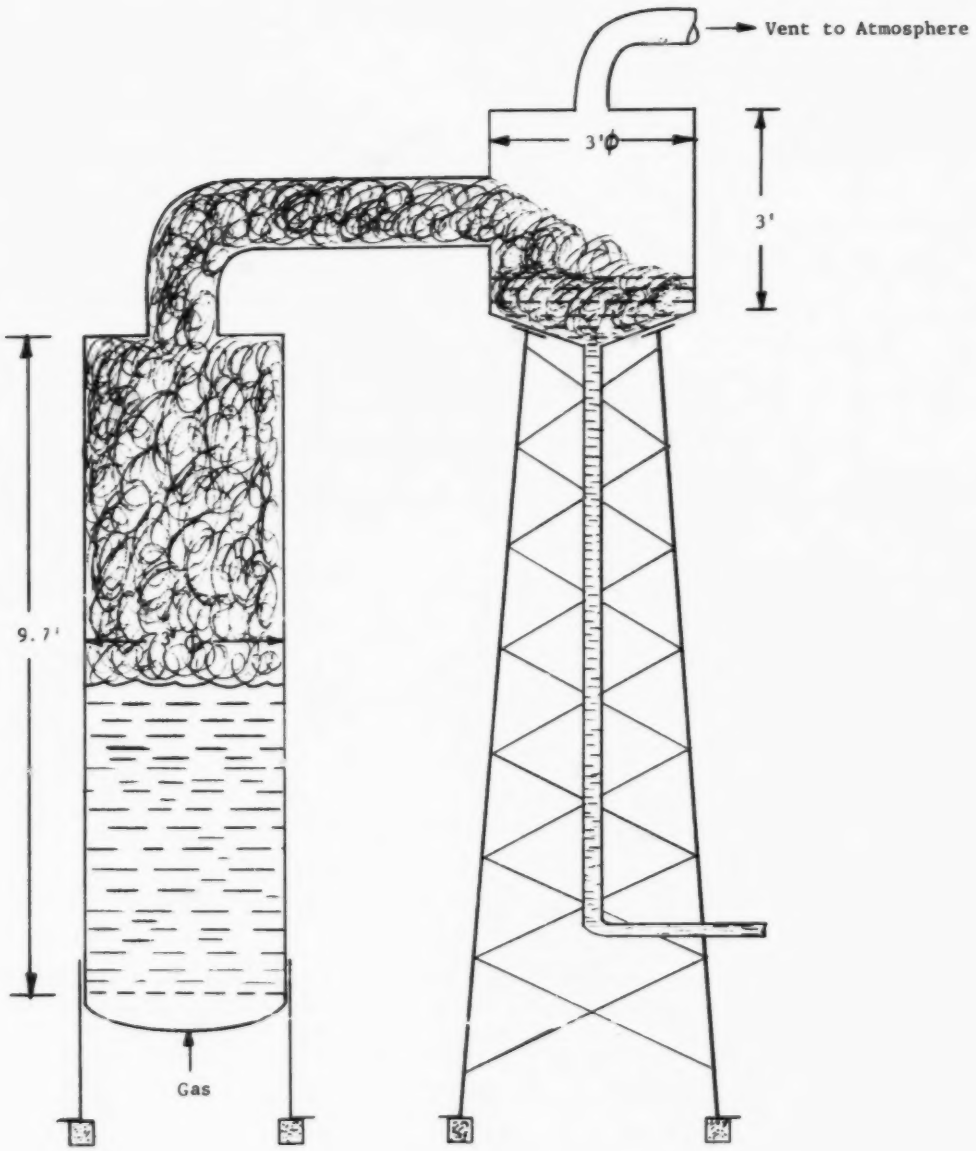
To design the foam column it was assumed that:

- The liquid in the column will expand by 15% due to the passage of gas through it. This factor was based on observation of the column behavior during the experimental work.
- The ratio of the height of the foam column to that of the liquid column just below it should be about 1:1. Experimental work discussed already showed that this ratio allows for satisfactory drainage of the liquid from the rising foam and, therefore, minimizes the amount of liquid rejected as foam.

- The diameter of the foam receiver is equal to that of the foaming column. Its height, however, is equal to about 1/3 that of the total foaming column. The foam receiver will be elevated and will rest on a structure similar to that on which city water tanks rest. A schematic diagram of a foaming column which can handle 108 x 10^3 GPD is shown (see Figure 24).

Figure 24

DESIGN OF A FOAM FRACTIONATION COLUMN FOR TREATING 108 x 10^3 GAL./DAY (75 GPM)



For handling 54 x 10^6 GPD of water, 6 towers each 15 ft. in diameter and 36 ft. high were used. Each two columns were connected to a foam receiver 21 ft. in diameter and 15 ft. high. A diagram showing this arrangement (elevation) is illustrated in Appendix Figure 8. Appendix Tables 36 and 37 show in detail the process basis specification data, and the dimensions of the foam columns used in making the designs.

It is realized that the designs described so far may not represent the most desirable or the most economical arrangements, especially since steel is used as a material of construction. The costs are included in this report, however, for orientation purposes. Less costly plants can be probably built if rectangular tanks are either built above the ground or embedded in the soil. Also, the use of concrete or timber (either one being reinforced) as materials of construction may reduce the capital investment.

Capital Costs

For each case estimates have been made of the capital costs. Some of these costs are rather high on the low capacity units but they decrease considerably. Detailed data showing the breakdown of cost estimates are shown in Appendix Table 38.

Operating Costs

The operating costs were worked out based on the Office of Saline Water recommended procedures. A complete breakdown of the operating costs in shown in Appendix Table 39. For plants of 10 and 100 million gals./day, the operating costs are 2.5 and 1.5¢/1000 gal., respectively.

Cost of Altering Waste Water pH Is Moderate

Foaming can remove about 95% of ABS present in secondary effluents at a pH of 6.5-7.5. COD removal is only about 20-40% at these pH levels, but it can be increased by altering waste water pH to higher or lower levels. Whether altering waste water pH to improve COD removal in large scale operation is feasible will depend on the cost and amount of acid or base used. Therefore, experiments were made to determine the amount of hydrochloric acid or sodium hydroxide that was required to alter the pH of three different samples of secondary effluent from the Bergen County Sewage Treatment Plant. The range of pH studied was rather narrow 5-9. Variations beyond this range will be probably considered rather drastic, and perhaps undesirable. The data are summarized below and more detailed results are shown in Appendix Table 40.

Waste Water Batch No.	Initial pH	Final pH	Milliequivalents/Liter Of HCl or NaOH to Alter pH
26	6.7	5.7	1.89
26	6.7	4.7	2.64
26	7.2	8.2	0.60
26	7.2	9.2	1.33
27	7.1	6.1	1.59
27	7.1	5.1	2.65
27	7.1	8.1	0.56
27	7.1	9.1	1.42
28	7.1	6.1	1.69
28	7.1	5.1	2.74
28	7.1	8.1	0.51
28	7.1	9.1	1.46

The cost of altering pH was calculated by assuming $0.05 per lb. of HCl and $0.079 per lb. of NaOH. The results of the calculation are shown below. (See Appendix Tables 39 and 40)

The data indicate that it will cost about 4¢/1000 gals. of water to alter pH from about 7 to 5, or 3.5¢ to alter pH from about 7 to 9. These costs are not excessive and it may be economical in some instances to alter waste water pH if the improvement in COD removal is appreciable and cheaper than can be achieved by other treatment methods, such as carbon adsorption.

It should be emphasized that the cost of altering pH will vary depending on the acidity or basicity of the waste water being treated. These numbers are only shown for orientation purposes (Figures 25 and 26).

Figure 25

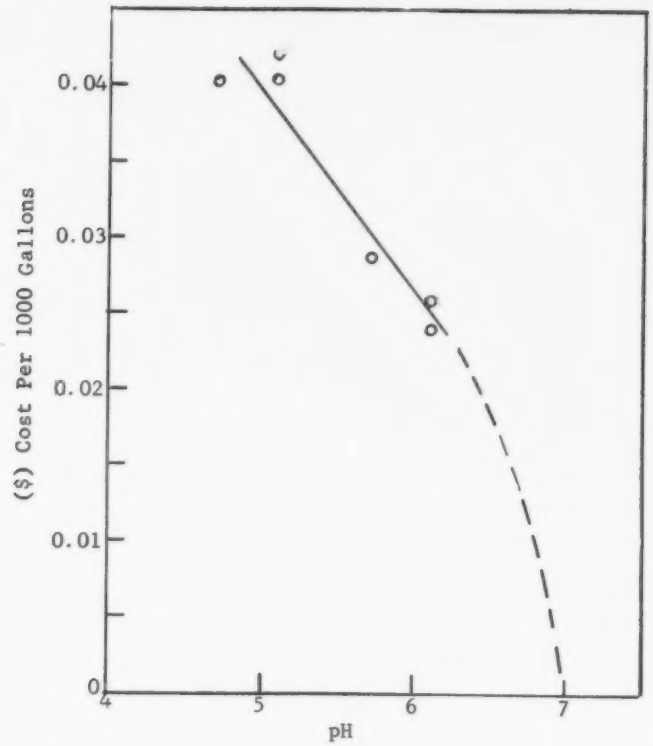
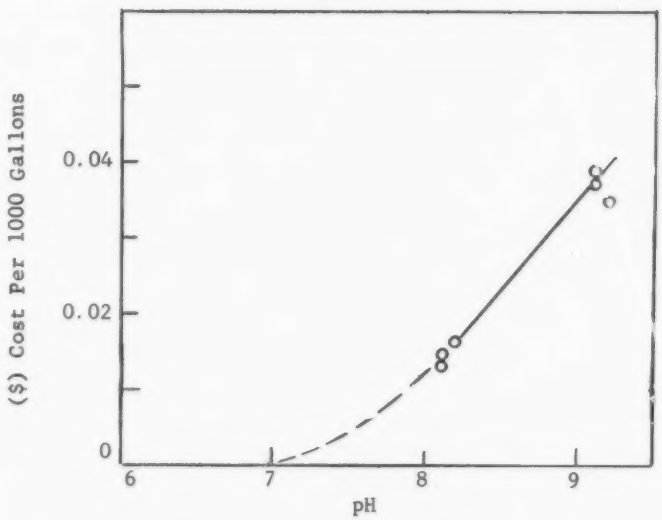


Figure 26



XI. RECOMMENDATIONS FOR FUTURE WORK

Future work on foam fractionation should be aimed at investigating the following points:

- Behavior of the system in large scale equipment.
- Defining the capacity of carbon adsorbents after foaming using long columns in series.
- Reproducibility of the additives action in improving COD removal.
- A study of the response of removal by foam fractionation to upsets in the system such as variation in feed concentration of soluble organics.

Preceding page blank

XII. PATENTABLE FEATURES

Two patent memoranda have been submitted. Abstracts of these are shown below.

PM 13778
PD 257-61
Cl. 25

R. M. Skomoroski
I. A. Eldib

PURIFICATION OF WASTE WATER BY FOAM FRACTIONATION IMPROVED BY ADDING BIODEGRADABLE DETERGENTS OR PROTEINS

Biodegradable materials are added to waste water to create foam and thus help remove low mol. wt., low surface active chemicals from polluted water by foam fractionation.

RIP
12/13/61

11/20/61

PM 20475
PD 54-62
Cl. 25

R. M. Skomoroski
I. A. Eldib

ALTERING pH OF WASTE WATER IMPROVES PURIFICATION BY FOAM FRACTIONATION

Waste water is foamed to remove almost all the detergents, and then pH of the foamed water is either increased or decreased by inorganic base or acid, and the water is foamed a second time to remove all the weakly surface active water soluble organics.

RIP
2/27/62

2/8/62

Preceding page blank

XIII. APPENDICES

	Page
APPENDIX A TABLES AND FIGURES	73-132
APPENDIX B COMPOSITION OF DETERGENTS	133
APPENDIX C EQUIPMENT	135
APPENDIX D SURFACE TENSION MEASUREMENTS	137
• Soluble Organics In Waste Water Decrease Water Surface Tension	137
APPENDIX E PREDICTION OF ENRICHMENT BY FOAM FRACTIONATION	141
• Surface Activity Increases With Increased Molecular Weight	141
• Basic Equations	143
• Example	144
APPENDIX F FOAM FRACTIONATION OF BARSTOW EFFLUENT (SANTE FE RAILROAD SHOPS, CALIFORNIA)	145
APPENDIX G REFERENCES	149

Preceding page blank

Preceding page blank

Appendix Table 1

ANALYTICAL DATA ON WASTE WATER EFFLUENTS

Date	Time	Batch #	Pretreatment	Effluent	ppm COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	pH	Corrected COD
1/16/61	10:00 a.m.	3	Filtered	Secondary	303	63*	63	490	5.3		192
1/28/61	9:30 a.m.	5	Unfiltered	Secondary	203	-	-	10			201
			Unfiltered	Aeration Tank	1745	-	-	360			1663
			Unfiltered	Primary	539	-	-	390			451
1/30/61	10:00 a.m.	6	Filtered	Secondary	174	5*	5	310	4.75		104
			Unfiltered	Secondary	277	81*	64	330	4.76		202
2/7/61	9:30 a.m.	8	Filtered	Secondary	192	10*	10	350	4.3		113
2/19/61	10:00 a.m.	9	Filtered	Primary	210	7*	7	290	1.5		144
			Filtered	Secondary	171	8*	8	320	2.56		99
2/21/61	9:30 a.m.	10	Filtered	Primary	119	13*	13	170	1.7		81
				Secondary	132	3*	3	160	3.5		96
2/27/61	9:45 a.m.	11	Unfiltered	Secondary	137	40*	26	130	5.0		108
			Centrifuged**	Primary	137	20*	14	160	2.36	6.8	101
			Centrifuged**	Secondary	130	13*	5	140	5.08		98
1/2/62	9:15 a.m.	12	Filtered	Primary	192	730	121	150	3.1		158
			Filtered	Secondary	116	505	88	110	5.0	7.4	91
1/4/62	6:45 a.m.	13	Filtered	Secondary	116	658	89	200	5.6	7.2	71
1/8/62	9:30 a.m.	14	Filtered	Secondary	36	375	82	70	2.28	7.4	20
1/10/62	9:30 a.m.	15	Filtered	Secondary	71	399	65	90	2.16	7.1	51
1/16/62	9:30 a.m.	16	Unfiltered	Secondary	68	612	81	160	3.54		32
			Filter Paper	Secondary		6*					
			Filter S.S.***	Secondary		13*					
1/24/62	10:00 a.m.	17	Filtered	Secondary	169	619	98	140	4.10	7.0	157
1/29/62	10:00 a.m.	18	Filtered	Secondary	132	506	80	130	4.22		103
2/1/62	8:00 a.m.	19	Filtered	Secondary	109	585	77	150	4.72		75
2/7/62	8:45 a.m.	20	Filtered	Secondary	128	788	109	240	4.10		74
2/14/62	9:15 a.m.	21	Filtered	Secondary	155	857	128	270	7.72	7.4	94
2/19/62	9:30 a.m.	22	Filtered	Secondary	114	587	99	150	4.88		80
3/5/62	11:00 a.m.	24	Filtered	Secondary	144	-	-	-	-		-
3/19/62	10:00 a.m.	26	Filtered	Secondary	70	410	75	70	2.84	7.9	54
3/21/62	10:00 a.m.	27	Filtered	Secondary	94	455	80	80	-	7.3	76
3/27/62	9:00 a.m.	28	Filtered	Secondary	87	497	89	100	5.70	7.8	64
4/9/62	10:00 a.m.	30	Filtered	Secondary	82	376	89	60	2.06	8.2	68
4/24/62 (Middlesex)	1:00 p.m.	1	Filtered	Primary	794	1291	429	210	4.70	7.5	746
4/26/62 (Bernardsville)	10:15 a.m.	1	Filtered	Secondary	71	250	52	30	4.70	7.8	64

Appendix Table 1 (Cont'd.)

Date	Time	Batch #	Pretreatment	Effluent	ppm					pH	Corrected COD
					COD	T.S.	V.S.	Cl	ABS		
5/1/62	9:15 a.m.	32	Filtered	Secondary	89(109)	581	78	110	3.56	7.6	74
5/4/62	9:30 a.m.	33	Filtered	Secondary	89(74)	586	80	120	2.56	7.5	54
5/8/62	10:00 a.m.	34	Filtered	Secondary	139(143)	641	123	150	2.05	8.1	107
5/11/62	10:00 a.m.	35	Filtered	Secondary	141(129)	668	117	160	4.86	7.6	99
5/23/62	10:00 a.m.	36	Filtered	Secondary	208(130)	835	105	230	4.12	7.7	112
5/28/62	9:30 a.m.	37	Filtered	Secondary	176(164)	790	111	250	5.90	-	113
5/31/62	10:00 a.m.	38	Filtered	Secondary	150(155)	604	107	130	4.06	7.2	124
6/4/62	10:00 a.m.	39	Filtered	Secondary	157	617	112	150	4.15	7.2	123
6/7/62	10:00 a.m.	40	Filtered	Secondary	182	780	145	260	3.85	7.4	123
6/11/62	10:00 a.m.	41	Filtered	Secondary	148(125)	554	123	150	5.45	7.6	102
6/13/62	10:00 a.m.	42	Filtered	Secondary	228(236)	757	131	220	5.40	7.5	182
6/18/62	10:00 a.m.	43	Filtered	Secondary	124(152)	612	106	170	3.88	7.4	100
6/21/62	9:30 a.m.	44	Filtered	Secondary	262(230)	990	150	310	4.15	7.0	176
6/25/62	10:00 a.m.	45	Filtered	Secondary	260	354	126	310(290)	3.16	7.3	192
7/2/62	10:00 a.m.	46	Filtered	Secondary	161(153)	691	125	170	4.05(3.38)	7.5	119

OD - Chemical Oxygen Demand
T.S. - Total Solids
V.S. - Volatile Solids
Cl - Chloride
ABS - Alkylbenzene Sulfonates

* Refers to total suspended solids; others are total dissolved solids.
** 1660 G for 30 minutes.
*** Filtered through porous steel disc.

Numbers in brackets refer to duplicate analyses.
All waste water samples were obtained from Little Ferry, N. J. except two samples which were obtained from Bernardsville and Middlesex County.

Appendix Table 2

SAMPLE CALCULATION OF ENRICHMENT RATIOS

V_o = Volume of liquid foamed, cc.

V_L = Volume of liquid in column after foaming, cc.

V_F = Volume of foam overhead, cc.

C_o = ppm of ABS or COD in unfoamed liquid (measured)

C_L = ppm of ABS or COD in foamed liquid (measured)

C_F = ppm of ABS or COD in foam overhead (calculated)

Material Balance:

$$V_oC_o = V_FC_F + V_LC_L$$

$$C_F = \frac{V_oC_o - V_LC_L}{V_F}$$

and, enrichment ratio = $\frac{\text{Concentration of ABS or COD in Foam (Calculated)}}{\text{Concentration of ABS or COD in Foamed Liquid (Measured)}}$

$$= \frac{C_F}{C_L}$$

Appendix Table 3

BATCH FOAM FRACTIONATION RUNS ON PRIMARY AND SECONDARY EFFLUENTS (BERGEN COUNTY)

Run No.	Feed	Foam Overhead, cc.	ppm Corrected COD	ppm Cl	ppm ABS	% Removal COD	% Removal ABS	Surface Tension Before	Surface Tension After	Surface Tension Foam
Secondary Effluent	Unfiltered	-		10	4.72	-	-			
7	Unfiltered	95	100	290	0.4	27	92	44.7	62.7	29.2
10	Filtered	120	69	290	0.1	49	98	51.5	64.2	30.0
Primary (Tank)	Unfiltered	-	451	390	1.8	-	-			
8	Unfiltered	15	353	370	0.6	22	67	54.0	62.4	29.4
12	Filtered	20	192	330	0.3	58	83	53.2	58.7	28.6

Gas Disperser: Fine
Time: 30 Min.
Air Flow Rate: 20.5×10^{-3} CF/Min. (STP)
Column Diameter: 2"
Feed To Foam Fractionation Unit: 1200 cc.
Temperature: 78°F.

Nominal Max. Pore Size (Microns)

Fine Gas Disperser: 4-5.5
Medium Gas Disperser: 10-15

T.S. refers to total (suspended) solids.
V.S. refers to volatile solids.

Appendix Table 4

VARYING COLUMN DIAMETER AND GAS BUBBLE SIZE IN BATCH FOAM FRACTIONATION RUNS

Run No.	Column Diameter	Gas Disperser	Foam Overhead, cc.	ppm Corrected COD	ppm T.S.**	ppm V.S.	ppm Cl	ppm ABS	Surface Tension Liquid	% Removal COD	% Removal ABS
Feed Sec. Eff.	-	-	-	113	10	10	350	4.3	45.6	-	-
22	2"	Medium	1	89	7	7	350	0.9	56.5	21	79
23	1-1/2"	Medium	1	129	10	10	400	0.8	59.7		81
24	3/4"	Medium	1	89	6	6	340	1.3	56.6	21	70
25	3/4"	Fine	1	81	8	8	340	1.2	53.3	28	72
26	2"	Fine	13	81	8	8	330	0.6	58.0	28	86

Temperature: 76°F.
Time: 10 Min.
Feed: Filtered
Air Flow Rate: 8.1×10^{-3} CF/Min. (STP)
Column Capacities:
2" Column Diam. 1200*cc.
1-1/2" Column Diam. 1000*cc.
3/4" Column Diam. 450*cc.

* Refers to liquid volumes, not column capacities.
** Total suspended solids.

Appendix Table 5

VARYING AIR FLOW RATES IN BATCH FOAM FRACTIONATION RUNS

Run No.	Air Flow Rate CF/Min.(STP)x10^3	Foam Overhead, cc	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	Surface Tension Dynes/Cm. Liq.	Surface Tension Dynes/Cm. Foam	% Removal COD	% Removal ABS
Feed											
Sec. Eff.		-	113	10	10	350	4.3	45.6	-	-	-
18	20.5	3.2	81	4	4	350	0.5	61.0	28.1	28	88
19	32.8	16	73	5	5	350	0.4	56.3	28.4	35	91
20	45.5	22	73	8	8	350	-	51.1	28.4	35	
21	70.4	24	65	9	7	340	0.4	56.9	28.8	43	91

Temperature: 76°F.
Column Diameter: 3/4"
Gas Disperser: Fine
Feed: Filtered, 450 cc.
Time: 10 Min.

Appendix Table 6

BATCH FOAM FRACTIONATION RUNS - pH AND TEMPERATURE EFFECT

Run No.	Column Diam.	Charge, cc.	pH	Foam Overhead cc.	Temp.[c] °F.	Corrected COD	T.S.	V.S.	Cl	ABS	% Removal COD	% Removal ABS
Feed												
Sec. Eff.	-	-	7.2			71	658	89	200	5.6	-	-
Sec. Eff.*	(5 cc.-20 Wt.% NaOH Added)		11.9			82						
Sec. Eff.*	(1 cc.-20 Wt.% NaOH Added)		10.1			82						
54[a]*	2" (Fine)	1200	(~7.2)	180	75	50	621	65	190	0.09	39	98
57[a]*	2" (Fine)	1200	(~7.2)	200	35	50	656	76	190	0.20	39	96
55[a]*	2" (Fine)	1200	9.9	172	75	50	763	24	200	0.14	39	98
56[a]*	2" (Fine)	1200	11.7	260	75	50	1396	30	200	0.14	39	98
Feed							S.S.					
Sec. Eff.**	-	-	~7	-	-	201	81	64	330	4.76	-	-
Sec. Eff.*	-	-	~7	-	-	98	5	5	310	4.75	-	-
14[b]**	2"	1200	~7	155	76	125	48	41	370	0.31	38	94
15[b]**	1-1/2"	1000	~7	25	37ø	159	70	56	340	1.6	21	67
16[b]*	1-1/2"	1000	~7	1	78	79	2	2	330	1.12	9	76

* Filtered Feed
** Unfiltered Feed
ø Temperature increased during run to 67°F.

[a] Gas Disperser: Fine
Time: 15 Min.
Air Flow Rate: 66.4×10^{-3} CF/Min. (STP)
T.S. = Total Dissolved Solids

[b] Gas Disperser: Medium
Time: 30 Min.
Air Flow Rate: 20.5×10^{-3} CF/Min. (STP)

[c] Foam fractionation column jacketed.

Appendix Table 7

BATCH FOAM FRACTIONATION RUNS - EFFECT OF TIME

Run No.	Time	Foam Overhead, cc.	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	-% Removal- COD	-% Removal- ABS
Feed Sec. Eff.	-	-	97	13	5	140	5.2	-	-
41	15 Min.	140	60	3	3	140	0.19	38	95
42	30 Min.	148	52	0	0	150	0.14	48	97
43	60 Min.	138	60	0	0	150	0.12	38	98

Feed: 1200 cc. Secondary Effluent, 75°F.
Centrifuged: 3000 RPM for 30 Min.
Air Flow Rate: 43.0×10^{-3} CF/Min. (STP)
Gas Disperser: Fine, Column Diameter, 2"
pH: 7
T.S.: Total Suspended Solids

Run No.	Time, Min.	Foam Overhead, cc.	ppm COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	-% Removal- COD	-% Removal- ABS	Total Organic Nitrogen, ppm
Feed Sec. Eff.	-	-	92				7.70	-	-	*
75	3	310	108	873	106	280	0.42	-	95	20
72	4	185	72	856	99	280	0.64	22	92	12
73	6	200	53	868	125	270	0.69	42	91	14
74	10	205	88	838	110	280	0.40	4.4	95	

Feed: Secondary Effluent, Filtered Through S.S. Filter
Column Diameter: 2"
Temperature: 75°F.
T.S. = Total Dissolved Solids

Charge: 1200 cc.
Gas Disperser: Fine
Air Flow Rate: 66.4×10^{-3} CF/Min. (STP)

* Sample lost.

Appendix Table 8

BATCH FOAM FRACTIONATION RUNS - EFFECT OF ADDITIVES

Run No.	Charge, cc.	pH	Additive	Foam Overhead, cc.	Temp. °F.	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.	-	7.4	-	-	-	20	375	82	70	2.28	-	-
	-	2.3	0.5 cc. H_2SO_4	-	-	35	-	-	-	-	-	-
58	1200	7.4	-	50	75	16	344	94	70	0.14	20	94
59	1200	2.3	0.5 cc. H_2SO_4	68	75	8	1111	729	70	0.14	60	95
60	1200	7.4	-	38	75							
61	1000	-	1 cc. ABS Soln.*	14	75	24	365	63	70	0.14	-	94
65	1200	7.4	-	60	75							
66	1000	-	3 cc. ABS Soln.	145	75	35	342	58	80	0.62	-	74
63	1200	7.4	-	47	75							
64	1000	-	5 cc. ABS Soln.	240	75	47	374	56	70	1.12	-	51

Gas Disperser: Fine; Column Diameter: 2"
Time: 15 Min.; Air Flow Rate: 66.4 x 10^{-3} CF/Min. (STP)

* ABS Soln.: 1 Vol.% Dodecyl Benzene Sulfonate (Solefonate)

Notes: All Feeds Are Filtered.
T.S. = Total Dissolved Solids.
H_2SO_4 - Reagent Grade, 98 Wt.%.

Run No.	Charge, cc.	pH	Additive	Foam Overhead, cc.	Temp. °F.	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.*	-	7	-	-	-	86	505	88	110	5.0	-	-
49*	1200	7	ABS (0.1 cc.)	680	75	82	459	69	100	1.74	4.6	65
50*	1200	7	Egg Albumin (0.2 g.)	415	75	218	532	116	130	0.03	-	99
51*	1200	11.2	ABS (0.1 cc.)	800	75	270	521	136	150	1.78	-	64
52*	1200	11.2	Egg Albumin (0.2 g.)	420	75	250	477	126	150	0.06	-	99
53*	1200	11.2		140	75	110	460	78	150	0.09	-	98

Gas Disperser: Fine
Column Diameter: 2"
Air Flow Rate: 43.0 x 10^{-3} SCF/Min. (STP)
ABS: Dodecyl Benzene Sulfonate (Solefonate) Commercial Material, 60% Active.
Time: 15 Min.
T.S.: Total Dissolved Solids.

* All Feeds Filtered.

Appendix Table 9

BATCH FOAM FRACTIONATION RUNS - EFFECT OF pH

Run No.	Additive	pH	Foam Overhead, cc.	ppm					-% Removal-	
				COD	T.S.	V.S.	Cl	ABS	COD	ABS
Feed Sec. Eff.	None	7.4	-	92	857	128	270	7.70	-	-
74	None	7.4	205	88	838	110	280	0.40	4.4	95
78	H_2SO_4	2.1	350	72	1495	520	280	0.07	22	99
79	H_2SO_4	2.6	340	88	1082	280	280	0.11	4.4	98
76	NaOH	9.9	340	60	996	107	280	0.17	35	98
77	NaOH	11.9	470	56	2316	504	290	0.10	39	99
83*	H_2SO_4	2.5	15	96	1202	334	270	0.07	-	99
81*	NaOH	10.5	None	84	1077	103	280	0.14	8.7	98

Feed: Secondary Effluent, Filtered Through Stainless Steel Filter.
Charge: 1200 cc.
Column Diameter: 2"
Gas Disperser: Fine
Temperature: 75°F.
Time: 10 Min.
Air Flow Rate: 66.4×10^{-3} CF/Min. (STP)

* Charge: 1000 cc. Sec. Effluent. Foamed First at pH = 7.4

Appendix Table 9 (Cont'd.)

Run No.	Foam Overhead cc.	pH	Temp., °F.	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	% Removal COD	% Removal ABS
Feed Sec. Eff.	-	(~7)	-	96	3	3	160	3.5	-	-
31	86	(~7)	55	118	3	3	170	0.8	-	77
32	725	4.0	55	216	0	0	180	0.14	-	96
33	145	10.4	75	264	24	12	210	0.16	-	95
Feed Primary Eff.	-	(~7)	-	81	13	13	170	1.7	-	-
36	42	(~7)	75	66	10	10	170	0.16	19	91
34	675	4.0	75	312	8	8	170	0.11	-	94
35	136	10.4	75	281	47	15	220	0.12	-	93

Gas Disperser: Fine
Time: 15 Min.
Air Flow Rate: 45.5×10^{-3} CF/Min. (STP)
pH Values in Brackets Are Estimated.
Column Diameter: 2"
Feed Charge: 1200 cc.

Appendix Table 9 (Cont'd.)

Run No.	Feed	Foam Overhead, cc.	Final pH Values	Temp., °F.	ppm Corrected COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	% Removal COD	% Removal ABS
Feed	Unfiltered	-	7.4	-	108	40	26	130	5.0	-	-
Sec. Eff.	Centrifuged	-	7.4	-	98	13	5	140	(~5.2)	-	-
	Centrifuged	-	10.1	-	277	62	21	170	5.3	-	-
41	Filtered	140	(~7)	75	61	3	3	140	0.19	43	95
37	Filtered	200	10.2	75	209	94	20	180	0.17	24	97
39	Centrifuged	170	10.2	75	135	47	47	180	0.23	51	96
Feed	Unfiltered	-	6.8	-	133	61	41	150	2.0	-	-
Primary Eff.	Centrifuged	-	6.8	-	101	20	14	160	2.36	-	-
	Centrifuged	-	11.2	-	726	27	13	190	2.36	-	-
38	Filtered	100	10.4	75	170	21	20	190	0.14	76	94
40	Centrifuged	66	10.2	76	186	38	14	160	0.33	74	85

1200 cc. of Waste Water
Gas Disperser: Fine
Air Flow Rate: 43.0×10^{-3} CF/Min. (STP)
pH Values After Foaming
Time: 15 Min.
Centrifuged: ~3000 RPM for 30 Min.
pH Adjusted With Buffer Solution
T.S. = Total Suspended Solids
2" Diameter Column

Appendix Table 10

EFFECT OF DETERGENTS ON COD REMOVAL

Run No.	Additive, cc.	Foam Overhead, cc.	---ppm---- COD	ABS	% Removal COD	ABS
Sec. Eff.-Feed	-	-	54	2.84	-	-
130	None	14	62	0.20	-	93
129	None	7	-	-		
	1 T	~0.1	-	-		
	3 T	~0.4	-	-		
	5 T	6.5	-	-		
	10 T	5.2	19	0.17	65	94
128	None	6	-	-		
	1 E	~0.1	-	-		
	3 E	~0.3	-	-		
	5 E	~0.4	-	-		
	10 E	5	-	-		
	15 E	19	27	0.07	50	97
127	None	6	-	-		
	1 D	~0.1	-	-		
	3 D	~0.4	-	-		
	5 D	~0.8	-	-		
	10 D	2	-	-		
	15 D	3	-	-		
	20 D	7	62	0.17	-	94

1200 cc. Secondary Effluent - Filtered, Cl = 70 ppm, pH = 7.9,
ABS = 2.84, T.S. = 410, V.S. = 75
63 x 10^{-4} SCF/Min. Air Flow Rate
T = Tergitol (Neutral)
E = Ethoquad (Cationic)
D = Duponol (Anionic)

Stock solution: 1 gram of detergent dissolved in 1000 cc. distilled water. Various amounts of this soln. added to waste water prior to foaming. Stock solution concentration 10^3 ppm.

$$\text{ppm of additive} = \frac{\left(\begin{array}{c}10^3 \text{ ppm of additive} \\ \text{in stock soln.}\end{array}\right) \times \left(\begin{array}{c}\text{cc. of stock} \\ \text{soln. added}\end{array}\right)}{\left(\begin{array}{l}\text{cc. of waste water foamed +} \\ \text{cc. of stock soln. added}\end{array}\right)}$$

Appendix Table 11

EFFECT OF ADDITIVES ON FOAMING OF WASTE WATER

Run No.	Additive, cc.	Foam Overhead, cc.	ppm COD	ppm ABS	% Removal COD	% Removal ABS	Additives
Sec. Eff.	-	-	69**	2.06	-	-	T - Tergitol
136	None	3	53, 100 (76)*	1.53	-	26	D - Duponol
138	None	0	-	-	-	-	E - Ethoquad
	1 (T)	0.2	-	-	-	-	S - Solefonate
	3 (T)	0.3	-	-	-	-	A - Egg Albumin
	6 (T)	0.5	-	-	-	-	Stock soln. prepared in
	11 (T)	7	49, 38 (43)	0.28	38	86	same manner as in Table 10.
139	None	0.2	-	-	-	-	
	1 (D)	0.1	-	-	-	-	
	3 (D)	0.2	-	-	-	-	
	6 (D)	0.5	-	-	-	-	Foam Fractionation Con-
	11 (D)	4	61, 53 (57)	0.39	17	81	ditions
140	None	0.4	-	-	-	-	
	1 (E)	0.1	-	-	-	-	1200 cc. filtered secondary
	3 (E)	0.1	-	-	-	-	effluent initially, 1000 cc.
	6 (E)	0.1	-	-	-	-	with additive present.
	11 (E)	0.4	-	-	-	-	10 min., 75°F., 2" column,
	16 (E)	10	49, 89 (69)	0.10	0	95	fine gas dispersion.
141	None	0.3	-	-	-	-	63 x 10^{-3} SCF/Min. Air
	1 (S)	0.1	-	-	-	-	Flow Rate
	3 (S)	0.4	-	-	-	-	Feed: pH = 8.2
	6 (S)	0.6	-	-	-	-	T.S. = 376 ppm
	11 (S)	5	34, 53 (43)	0.99	38	52	V.S. = 89 ppm
142	None	2	-	-	-	-	Cl = 60 ppm
	1 (A)	0.02	-	-	-	-	N = 15 ppm
	3 (A)	0.02	-	-	-	-	
	6 (A)	0.05	-	-	-	-	COD values in parentheses
	11 (A)	0.1	-	-	-	-	are averages of two analy-
	21 (A)	0.1	-	-	-	-	ses.
	41 (A)	3	73, 69 (71)	0.16	-	92	

Additives were added in small portions until several cc.'s of foam were collected. For example, total amount of additive added in run 140 was 37 cc.'s of Ethoquad.

* Duplicate results for COD. Numbers in parentheses refer to average values.
** Duplicate sample lost.

Appendix Table 12

EFFECT OF VARYING FOAM LIQUID HEIGHT IN FOAM FRACTIONATION COLUMN

Run No.	Liquid Foamed, cc.	Foam Overhead, cc.	% of Liquid Collected as Collapsed Foam	Ht. of Foam, Inches	Ht. of Liquid, Inches	Height of Foam to Height of Liquid	---ppm---- ABS	COD	% Removal ABS	COD
Sec. Eff.		-	-	-	-	-	3.72	119	-	-
1	1000	10	1	7	5.5	1.275	0.81	83	78	30
2	2000	195	9.8	1.5	11	0.136	0.57	95	85	20
3	3000	30	1	15.4	16.5	1	0.61	115	84	3.4
4	4000	140	3.5	11	22	0.5	0.53	83	86	30
5	5000	220	4.4	4	29	0.138	0.50	121	87	-

Filtered Secondary Effluent: Cl = 170 ppm, T.S. = 691, V.S. = 125, pH = 7.5.
4" Diameter Column
Fine Gas Disperser, 75°F., Residence Time = 5 Min.
Air Flow Rate = 108 x 10^{-3} SCF/Min.
Batch Operation

Appendix Table 13

FOAM FRACTIONATION OF FOAM OVERHEAD

Run No.	Liquid Foamed, cc.	Foam Overhead, cc	------ppm------ COD	ABS	-% Removal- COD	ABS
Sec. Eff.	-	-	64(84)	3.56	-	-
164 A	1200	20	49(72)	0.74	19	79
165 A	8400	260	57(57)	0.65	23	82
166 B	260*	190	161	10.5	-	-
167 B	190**	125	274	67.8	-	-

A: 2" Diameter Column, Fine Gas Disperser
B: 3/4" Diameter Column, Medium Gas Disperser

Secondary Effluent: pH = 7.6, T.S. = 581, V.S. = 78, Cl = 110

* Foam Overhead From Run 165A Refoamed.
** Foam Overhead From Run 166B Refoamed.

10 Min. - Foaming Time
Air Flow Rate = 63×10^{-3} SCF/Min.
Numbers in brackets refer to duplicate analyses.

Appendix Table 14

BATCH FOAM FRACTIONATION RUNS - EFFECT OF REFLUX

Run No.	Reflux Time (Min.)	Foam Overhead, cc.	ppm COD	ppm T.S.	ppm V.S.	ppm Cl	ppm ABS	-% Removal- COD	-% Removal- ABS
Secondary Effluent	-	-	104	506	80	130	4.22	-	-
69	15	65	42	517	67	120	0.23	60	95
70	30	68	81	513	76	120	0.34	22	92
71	60	63	92	519	90	130	0.31	12	93

Secondary Effluent: Filtered
Temperature: 75°F.
Charge: 1200 cc.
Gas Disperser: Fine
Air Flow Rate: 66.4×10^{-3} CF/Min. (STP)

Run Number	Reflux Time (Min.)	Foam Overhead, cc.	ppm COD	ppm ABS	-% Removal- COD	-% Removal- ABS
Feed-Sec. Effluent		-	114(91)	5.45	-	-
196	0	20	91(110)	0.49	1	91
197	15	6	110(87)	0.40	3	92
198	15	82	52(48)	0.40	51	92

Experimental Conditions:

1200 cc. Secondary Effluent, Filtered
2" Column Diameter, Fine Gas Disperser
75°F., 5 Min. Foaming Time at End of
Reflux Period. Air Flow Rate = 63×10^{-3} SCF/Min.
Numbers in brackets refer to duplicate analyses.

Appendix Table 15

FOAM FRACTIONATION WITH OZONE-AIR MIXTURES

Run No.	Foam Overhead, cc.	pH	Ozone, ppm	ppm COD	ppm ABS	ppm Cl	ppm T.S.	ppm V.S.	% Removal COD	% Removal ABS
Sec. Eff.	-	8.1	-	108(112)	2.05	150	641	123	-	-
177	36	8.3	0	108(94)	0.46	140	613	111	10	78
176	30	-	5	104(136)	0.39	150	633	118	-	81
175	35	-	10	136(132)	0.60	150	636	126	-	71
174	15	-	20	131(131)	0.52	100	632	126	-	75
178	5	8.3	40	63(79)	0.[illegible]	140	610	105	35	96
173	5	-	53	100(92)	0.11	-	-	-	13	94

1200 cc. Secondary Effluent
2" Diameter Column
Fine Gas Disperser
75°F.
Air Flow Rate: 22×10^{-3} SCF/Min.
Foamed With Air-O_3 for 10 Minutes,
Then System Purged With N_2.

Numbers in brackets refer to duplicate analyses.

Appendix Table 16

EFFECT OF DIFFERENT AERATION GASES IN FOAMING

Run No.	Gas	Foam Overhead, cc	-----ppm------ COD	ABS	---% Removal--- COD	ABS
Sec. Eff. (Bernardsville)		-	65	4.70	-	-
159	N_2	12	53	0.39	18	92
163	N_2	22	13	0.41	80	91
158	Air	15	45	0.44	31	91
162	Air	23	25	0.35	61	93
161	O_2	25	73	0.41	-	91
160	O_2	20	65	0.35	-	93
Primary Eff. (Middlesex County)		-	746	4.70	-	-
156	N_2	470	706	1.18	5	75
155	Air	470	675	1.08	9	77
157	O_2	510	667	0.97	10	79

Bernardsville Sewerage Authority

pH = 7.8
T.S. = 250
V.S. = 52
Cl = 30
Chlorine Treated Secondary Effluent (Filtered).

Middlesex County Sewarage Authority

pH = 7.5
T.S. = 1291
V.S. = 429
Cl = 210
Primary Effluent (Filtered).

Experimental Conditions

1200 cc. waste water.
75°F., 2" column, fine disperser.
63 x 10^{-3} SCF/min. gas flow rate.

Appendix Table 17

EFFECT OF OXYGEN ON COD REMOVAL

Run No.	Gas	Foam Overhead	ppm COD	% Removal COD
Sec. Eff.	-	-	110	-
88	O_2	50	-	
	O_2	30	-	
	O_2	24	94	15
86	N_2	42	-	
	N_2	18	-	
	N_2	8	78	29
87	Air	72	-	
	Air	40	-	
	Air	16	86	22

1200 cc. Secondary Effluent, Filtered
Fine Gas Disperser
72°F., Cl $\sim$ 150 ppm
Effluent Foamed Three Times and Foam Returned to Original Liquid Twice.
63×10^{-3} SCF/Min. Gas Flow Rate

Appendix Table 18

FOAM FRACTIONATION WITH OZONE-AIR MIXTURES

Run No.	Foam Overhead, cc.	pH	Ozone, ppm	ppm COD	ppm ABS	ppm Cl	ppm T.S.	ppm V.S.	% Removal COD	% Removal ABS
Sec. Eff.	-	7.7	-	105(93)	4.86	160	668	117	-	-
182	15	8.2	0	73(50)	0.08	200	617	82	38	98
181	12	8.1	5	81(50)	0.69	150	652	106	34	86
180	10	8.0	10	89(38)	0.07	150	645	115	36	98
179	20	8.0	20	42(61)	0.10	150	638	113	48	98

900 cc. Secondary Effluent
2" Column Diameter
Fine Gas Disperser, 75°F.
Air Flow Rate: 28×10^{-3} SCF/MIN.
Foamed With AIR-O_3 For 10 Minutes,
Then System Purged With N_2.

Numbers in brackets refer to duplicate analyses.

Appendix Table 19

FOAM FRACTIONATION OF VARIOUS DETERGENTS

Run No.	pH	Additive	Foam Overhead, cc.	ppm ABS	% Removal ABS
Feed - Tergitol*			-	-	-
124	6.2	Tergitol	298	-	-
123	6.6	Tergitol	305	-	-
122	6.6	Tergitol	295	-	-
121	6.6	Tergitol	310	-	-
114	6.6	Tergitol	315	-	-
Average			304	-	-
120	2	Tergitol	310	-	-
119	11.9	Tergitol	315	-	-
Feed - Ethoquad*			-	-	-
113	6.7	Ethoquad	325	-	-
118	2	Ethoquad	325	-	-
117	11.9	Ethoquad	122	-	-
Feed - Duponol			-	20.0	-
112	5.6	Duponol	5	1.57	93
116	2	Duponol	25	2.50	88
115	11.9	Duponol	30	5.65	71

1000 cc. Distilled Water, 74°F.
Fine Gas Disperser
63×10^{-4} SCF/Min. Air Flow Rate

* ABS analytical method does not determine these detergents.

Tergitol (Uncharged) - Nonyl Phenyl Polyethylene Glycol Ether
Ethoquad (Cationic R^+Cl^-) - Polyethoxy Stearyl Methyl Ammonium Chloride
Duponol (Anionic R^-Na^+) - Sodium Lauryl Sulfate

Detergent stock solutions prepared in same manner as in Table 10. Stock solution concentration 10^3 ppm.

Appendix Table 20

EFFECT OF pH ON FOAM FRACTIONATION OF
DODECYL BENZENE SULFONATE AND EGG ALBUMIN SOLUTIONS

Run No.	pH	Additive	Foam Overhead, cc.	---ppm--- ABS	N	-% Removal- ABS	N
Feed - H_2O		ABS	-	14.2	-	-	-
109	6.6	ABS	82	6.50	-	54.2	-
111	2.0	ABS	80	0.78	-	94.5	-
110	2.4	ABS	35	1.08	-	92.4	-
107	11.5	ABS	145	2.13	-	85.0	-
108	11.9	ABS	125	1.03	-	92.7	-
Feed - H_2O			-	-	1.5	-	
104	6.8	EA	0	-	1.4	-	0
106	1.9	EA	100	-	< 1	-	> 33
105	2.2	EA	90	-	< 1	-	> 33
102	11.5	EA	7	-	< 1	-	> 33
103	12.0	EA	112	-	< 1	-	> 33

900 cc. Distilled Water
ABS - Dodecyl Benzene Sulfonate, pH = 6.6 (Solefonate)
EA - Egg Albumin, pH = 6.8
74°F.
63×10^{-4} SCF/Min. Air Flow Rate
pH Altered by Adding NaOH or H_2SO_4
N = Total Organic Nitrogen

Detergent and egg albumin stock solutions prepared in same manner as in Table 10. Stock solution concentration 10^3 ppm.

Appendix Table 21

FOAM FRACTIONATION OF SYNTHETIC DETERGENT SOLUTIONS OF LOW CONCENTRATIONS

Run No.	Foam Overhead, cc	Vol.%	ppm ABS	% Removal ABS	C_F/C_L ABS	---Foam Stability Tests*----- Foam Stability	Foam Vol., cc	Surface Tension, 75°F. dynes/cm.
Feed #2	-		1.51	-	-	3 Sec.	4	67.0
6	2	0.8	0.99	34.4	789			
Feed #3	-		2.43	-	-	4 Sec.	5	61.8
7	4	0.16	1.89	22.2	215			
Feed #4	-		8.04	-	-	5.5 Min.	10	58.3
8	30	1.0	2.07	74.3	289			

4" Diameter Column, 75°F.,
Fine Gas Disperser,
3000 cc. Distilled Water + Added
Solefonate, 3 Min. Aeration Time,
Air Flow Rate = 108×10^{-3} SCF/MIN.
Batch Operation.

* 50 cc. of Solution Shaken in 100 cc. Graduated Cylinder for 30 Seconds.

Appendix Table 22

INTERACTION OF DETERGENTS AND PROTEINS GIVES MORE FOAM

Run Number	Additive, cc.	Foam Overhead, cc.
90	None	0
93	15 (S)	0.9
94	30 (S)	1
95	40 (S)	75
91	10 (A)	0
96	40 (A)	0.2
92	10 (A), 5 (S)	0
97	40 (A), 40 (S)	144

1000 cc distilled water, pH~7
10 min., 77°F., 2 " diameter column, fine gas disperser
63×10^{-3} SCF/Min. air flow rate
S-Solefonate, A-Egg Albumin

Detergent and egg albumin stock solutions prepared in same manner as in Table 10. Stock solution concentration 10^3 ppm.

Appendix Table 23

EFFECT OF pH ON PROTEIN REMOVAL BY FOAMING

Run No.	pH	Foam Overhead, cc.	ppm COD	% Removal COD	Enrichment Ratio, C_F/C_L COD
Feed[a]	-	-	58	-	-
143	2.2	105	43	26	4.3
144	1.9	100	31	46	9.7
147	6.8	None	62	-	-
145	11.5	None	58	0	1
146	12.0	30	58	0	1
148*	12.0	34	58	0	1
149**	12.0	48	55	5	2.1

a) 1000 cc. distilled water, 40 cc. egg albumin soln.
75°F., 10 min., 2" diameter column, fine gas disperser
63×10^{-3} SCF/min. air flow rate
pH altered using H_2SO_4 or NaOH.
Egg albumin stock solution prepared in same manner as in Table 10. Stock solution concentration 10^3 ppm.

* N_2
** O_2, others, air.

Appendix Table 24

REMOVAL OF ABS AND PROTEINS BY FOAMING

Run No.	Foam Overhead, cc.	pH	ppm			% Removal			Enrichment Ratio, C_F/C_L	
			COD	ABS	N	COD	ABS	N	COD	ABS
Distilled water + additives			58	9.40	7	-	-	-	-	-
151	132	11.9	23	0.67	6	60	93	14	12	99
152	112	11.5	34	0.91	8	41	90	-	7.3	84
153	218	2.4	23	0.50	6	60	95	14	7.9	82
154	135	2.0	15	0.54	5	74	94	28	22	122

Stock solutions prepared in same manner as in Table 10. Stock solution concentration 10^3 ppm. 40 cc. of Solefonate stock solution and 40 cc. of egg albumin stock solution added to distilled water here.
1000 cc. distilled water
10 min., 75°F., 2" diameter column, fine gas disperser
63×10^{-3} SCF/Min. air flow rate
pH altered using H_2SO_4 or NaOH

Appendix Table 25

SUMMARY OF CONTINUOUS RUNS

Volume of Liquid in Column = 1000 cc.
Residence Time = 3 Minutes

Run No.	Air Flow Rate, SCF/Min.	$C_{eqm.}/C_o$ ABS	$C_{eqm.}/C_o$ COD	Air Liquid Ratio, SCF/Gal.
6	63×10^{-3}	0.18	0.63	0.72
7	32×10^{-3}	0.29	1.0	0.36
8	45×10^{-3}	0.13	0.56	0.52
9	63×10^{-3}	0.12	0.58	0.72

Air Flow Rate = 63×10^{-3} SCF/Min.
Volume of Liquid in Column = 1000 cc.

Run No.	Residence Time, Min.	$C_{eqm.}/C_o$ ABS	$C_{eqm.}/C_o$ COD	Air Liquid Ratio, SCF/Gal.
2	5	0.17	0.95	1.14
3	2	0.41	0.94	0.49
4	2.5	0.18	0.92	0.60
5	2.5	0.12	0.79	0.60
6	3	0.18	0.63	0.72
9	3	0.12	0.58	0.72

Residence Time = 3 Minutes
Air Flow Rate = 108×10^{-3} SCF/Min.

Run No.	Volume Of Liquid In Column, cc.	$C_{eqm.}/C_o$ ABS	$C_{eqm.}/C_o$ COD	Air Liquid Ratio, SCF/Gal.
12	2000	0.20	0.89	0.61
13	3500	0.36	0.89	0.35

Appendix Table 26

DETAILED DATA ON CONTINUOUS RUNS

Run No.	Residence Time, Min.	Waste Water Volume, cc.	Liquid ppm COD	Liquid ppm ABS	Foam Overhead ppm COD	Foam Overhead ppm ABS	Foam Overhead Volume, cc.	% Removal COD	% Removal ABS
1	5	Feed	113	5.90				-	-
		200	98	0.60				13	90
		600	104	0.58				8	90
		1400	107	0.55				5	91
		2020	71	0.52				37	91
		2620	99	0.52				12	91
		3200	74	0.56				35	91
		3800	69	0.54			15	39	91
2	5	Feed	123	4.06				-	-
		250	123	-				0	-
		1250	113	0.69				8	83
		2500	128	0.67				-	84
		3750	-	0.84				-	79
		5000	111	0.70			72	10	83
3	2	Feed	123	4.15				-	-
		1000	138	1.56				-	62
		2000	126	-				-	-
		3000	115	1.72				6.5	59
		4000	98	-				20	-
		5000	111	-				10	-
		6000	102	1.60				17	62
		7000	111	-				10	-
		8000	139	-				-	-
		9000	111	1.68				10	60
		10,000	118	-	1240	202	137	4	-
4	2.5	Feed	123	3.85	-			-	-
		4800	115	0.64	1323	20.2		6.5	83
		7600	119	0.70	1066	71	70	3	82
		9600	111	0.76	-	-		10	80
		11,600	112	0.70	-	-		9	82
		13,600	111	0.56	-	-	78	10	85
							148 Total		
5	2.5	Feed	123	3.85	-	-	-	-	-
		4000	-	-	837	33.8	78	-	-
		10,000	99	0.50	1195	92	90	19	87
		16,000	-	-	1595	21.9	67	-	-
		22,000	95	0.41	1362	286	70	23	89
							305 Total		
6	3	Feed	102	5.45	-	-	-	-	-
		5000	60	1.00	-	348	64	41	82
		10,000	62	0.91	1693	-	56	39	83
		15,000	-	-	-	370	64	-	-
		20,000	-	0.97	1700	-	60	-	82
		25,000	66	-	388	-	55	35	-
							299 Total		
7	3	Feed	102	5.45	-	-	-	-	-
		5000	98	1.09	-	405	45	4	80
		10,000	-	1.36	1732	-	45	-	75
		15,000	94	-	-	430	45	8	-
		20,000	-	1.60	1790	-	43	-	71
		25,000	110	-	-	510	43	-	-
		30,000	-	1.64	1860		45	-	70
							366 Total		

Appendix Table 26 (Cont'd.)

Run No.	Residence Time, Min.	Waste Water Volume, cc.	Liquid ppm COD	Liquid ppm ABS	Foam Overhead ppm COD	Foam Overhead ppm ABS	Foam Overhead Volume, cc.	-% Removal- COD	-% Removal- ABS
8	3	Feed	182	5.40	-		-	-	-
		5000	85	0.67	-		55	53	88
		10,000	77	0.71	1855		55	58	87
		15,000	-	-	-		58	-	-
		20,000	-	0.68	1696		60	-	87
		25,000	125	-	-		68	31	-
		30,000	-	0.74	2034		60	-	86
							356 Total		
9	3	Feed	182	5.40	-	-	-	-	-
		5000	-	0.62	-	340	55	-	89
		10,000	-	0.67	1657	-	57	-	88
		15,000	144	-	-	-	65	21	-
		20,000	-	0.62	-	-	70	-	89
		25,000	113	-	-	-	65	38	-
		30,000	-	0.64	1716	-	65	-	88
		35,000	97	-	-	305	40	47	-
							417 Total		
10	3.8	Feed	100	3.88	-	-	-	-	-
		7200	94	1.18	5436	510	20	4	70
		14,400	106	1.28	3066	249	31	-	67
		21,600	106	1.18	3216	198	28	-	70
		28,800	126	1.06	3611	211	28	-	73
							107 Total		
11	5	Feed	192	3.16				-	-
		3000	-	-				-	-
		12,000	-	-			25	-	-
		21,000	-	-			17	-	-
		30,000	146	0.74			18	24	76
							60 Total		
12	3	Feed	119	3.72				-	-
		2666	110	0.93				7.5	75
		3998	98	0.89				18	76
		5330	122	0.75				-	80
		6662	98	0.77				18	80
		7994	98	-				18	-
		9326	-	0.67			25	-	82
13	3	Feed	119	3.72				-	-
		5832	122	1.09				-	71
		8164	90	-				24	-
		10,496	122	1.38				-	-
		12,828	-	1.35		608		-	64
		15,160	106	1.33		585	80	11	62

Run No.	Batch No.	Air Flow Rate, SCF/Min.	Volume Of Liquid in Column, cc.	Feed Rate, cc./Min.	Column Diameter, in.	A	B
1	37	63×10^{-3}	500	100	2	7	19
2	38	63×10^{-3}	1000	200	2	19	6.5
3	39	63×10^{-3}	1000	500	2	19	6.5
4	40	63×10^{-3}	1000	400	2	19	6.5
5	40	63×10^{-3}	1000	400	2	19	6.5
6	41	63×10^{-3}	1000	333	2	19	6.5
7	41	32 "	1000	333	2	19	6.5
8	42	45 "	1000	333	2	19	6.5
9	42	63 "	1000	333	2	19	6.5
10	43	108 "	2740	720	4	10	17.5
11	45	108 "	3000	600	4	10	16.5
12	46	108 "	2000	666	4	10	22
13	46	108 "	3500	1166	4	10	13.5

A - Distance in inches between inlet and outlet of waste water to column.
B - Distance in inches between liquid surface in column and foam overhead outlet.

Appendix Table 27

CALCULATION OF AVERAGE ABS CONCENTRATION IN FOAM FRACTIONATION COLUMN (MODEL I)

$\bar{t}$ Min.	5				2			
F cc./Min.	200				500			
P cc./Min.	190				475			
V cc./Min.	10				25			
V_R cc	1000		1000		1000		1000	
$C_F = \bar{C}_o$ mg/L	2		5		2		5	
C_P mg/L	0.5		0.5		0.5		0.5	
p mg/L/Min.	0.095		0.095		0.2375		0.2375	
f mg/L/Min.	0.4		1		1		2.5	
k_1	10	50	10	50	10	50	10	50
k	0.1	0.5	0.1	0.5	0.25	1.25	0.25	1.25
B = (p -f)	-0.305	-0.305	-0.905	-0.905	-0.7625	-0.7625	-2.2625	-2.2625
B/k	-3.05	-0.61	-9.05	-1.81	-3.05	-0.61	-9.05	-1.81
t Min.	$\bar{C}$ mg/L							
1	2.10	1.45	5.39	3.74	2.23	1.01	5.89	2.72
2	2.19	1.12	5.73	2.98	2.41	0.72	6.59	2.07
3	2.27	0.92	6.05	2.52	2.55	0.64	7.14	1.89
4	2.34	0.80	6.34	2.24	2.66	0.62	7.56	1.83
5	2.41	0.72	6.59	2.07	2.75	0.61	7.89	1.81
6	2.47	0.68	6.83	1.97	2.82	0.61	8.15	1.81
7	2.53	0.65	7.04	1.91	2.87	0.61	7.89	1.81
8	2.58	0.64	7.23	1.87	2.91	0.61	8.50	1.81
9	2.62	0.63	7.40	1.85	2.94	0.61	8.62	1.81
10	2.66	0.62	7.56	1.83	2.96	0.61	8.72	1.81

Appendix Table 28

CALCULATION OF AVERAGE ABS CONCENTRATION IN FOAM FRACTIONATION COLUMN (MODEL II)

$\bar{t}$ Min. / F cc./Min. / P cc./Min. / V cc./Min. / V_R cc.	5 / 200 / 190 / 10 / 1000		5 / 200 / 190 / 10 / 1000		2 / 500 / 475 / 25 / 1000		2 / 500 / 475 / 25 / 1000		2 / 500 / 487.5 / 12.5 / 1000	
C_F mg/L $C_o = \frac{k_1 c}{}$ $\frac{C_P}{C_o} = c$	2 - - 2		5 - - 5		2 - - 2		5 - - 5		5 - - 5	2 - - 2
f	0.4		1		1		2.5		2.5	1
k_1	10	50	10	50	10	50	10	50	50	50
$k = \frac{V}{V_R} k_1$	0.1	0.5	0.1	0.5	0.25	1.25	0.25	1.25	0.625	0.625
$D = P/V_R$	0.19	0.19	0.19	0.19	0.475	0.475	0.475	0.475	0.4875	0.4875
$(D + k)$	0.29	0.69	0.29	0.69	0.725	1.725	0.725	1.725	1.1125	1.1125
$f/(D + k)$	1.379	0.580	3.448	1.449	1.379	0.580	3.448	1.449	2.247	0.8989
t Min.	$\bar{c}$ mg/L									
1	1.84	1.29	4.61	3.23	1.68	.83	4.19	2.08	3.15	1.26
2	1.73	.94	4.32	2.34	1.52	.63	3.81	1.56	2.54	1.02
3	1.64	.76	4.09	1.89	1.45	.59	3.62	1.47	2.34	0.94
4	1.57	.67	3.93	1.67	1.41	.58	3.53	1.45	2.28	0.91
5	1.52	.63	3.81	1.56	1.39	.58	3.49	1.45	2.26	0.90
6	1.49	.60	3.72	1.51	1.39	.58	3.47	1.45	2.25	0.90
7	1.46	.59	3.65	1.48	1.38	.58	3.46	1.45	2.25	0.90
8	1.44	.59	3.60	1.46	1.38	.58	3.45	1.45	2.25	0.90
9	1.42	.58	3.56	1.46	1.38	.58	3.45	1.45	2.25	0.90
10	1.41	.58	3.53	1.45	1.38	.58	3.45	1.45	2.25	0.90

Appendix Table 29

COMPARISON OF ABS AND COD CONCENTRATIONS IN FEED AND FOAM OVERHEAD

Run No.	--Feed, ppm--- ABS	COD	Foam -Overhead, ppm- ABS	COD	--$C_{overhead}/C_{Feed}$--- ABS(a)	COD(b)
3	4.15	123	202	1206	48.7	9.8
4	3.85	123	20.2	1264	5.2	10.3
4	3.85	123	71	1007	18.4	8.2
5	3.85	123	33.8	778	8.8	6.3
5	3.85	123	92	1136	23.7	9.2
5	3.85	123	21.9	1536	5.7	12.5
5	3.85	123	286	1303	74.3	10.6
6	5.45	102	348	1659	63.9	16.3
6	5.45	102	370	1666	67.9	16.3
6	5.45	102	-	354	-	-
7	5.45	102	405	1698	74.3	16.6
7	5.45	102	430	1756	78.9	17.2
7	5.45	102	510	1826	93.6	17.9
8	5.40	182	-	1805	-	9.9
8	5.40	182	-	1646	-	9.0
8	5.40	182	-	1984	-	10.9
9	5.40	182	340	1607	63.0	8.8
9	5.40	182	305	1666	56.5	9.2
10	3.88	100	510	5398	131.4	54.0
10	3.88	100	249	3028	64.2	30.3
10	3.88	100	198	3178	51.0	31.8
10	3.88	100	211	3573	54.4	35.7
13	3.72	119	608	-	163.4	-
13	3.72	119	585	-	157.3	-

(a) This column gives an indication of the range of values which k_1 can have in the mathematical models of foam fractionation. These values apply to ABS and the values in column (b) refer to COD.

Appendix Table 30

ADSORPTION ON ACTIVATED CARBON

Run No.:	7A	8A
Feed Pretreatment:	Filtered & Foamed	Filtered
Activated Carbon:	1.6 Gms. (5 cc.)	1.6 Gms. (5 cc.)

Time (Min.)	COD, ppm	Waste Water, Vol. in cc.	Time (Min.)	COD, ppm	Waste Water, Vol. in cc.
0	Feed: 137	0	0	Feed: 198	0
42	87	25	32	0	25
105	-	50	83	-	50
139	-	75	118	-	75
175	-	100	148	-	100
207	18	125	172	48	125
245	-	150	205	-	150
292	-	175	242	-	175
324	-	200	269	-	200
351	-	225	307	-	225
385	(-17)	250	344	107	250
408	-	275	380	-	275
457	-	300	425	-	300
479	-	325	456	-	325
519	-	350	482	-	350
546	48	375	507	78	375
597	-	400	546	-	400
629	-	425	589	-	425
663	-	450	628	-	450
707	-	475	667	-	475
-	(-17)	500	-	107	500

75°F., Secondary Effluent
Surface Area = 1408 m^2/g.
Pore Volume = 0.799 cc.
Pore Radius = 11 Å
(Pittsburgh Activated Carbon, Type RB Pulverized)
Foam Fractionation Conditions: 1200 cc. Sec. Effluent, 75°F., 2" Diam. Column, Fine Gas Disperser, 15 Min., Air Flow Rate: 66.4 x 10^{-3} CF/Min. (STP)

Appendix Table 31

ADSORPTION ON ACTIVATED CARBON

Run No.:	13A	14A
Feed Pretreatment:	Filtered	Filtered and Foamed
Activated Carbon:	35.2 g. (100 cc.) (Cl = 150 ppm)	33.2 g. (100 cc.) (Cl = 150 ppm)

Time, (Min.)	COD	T.S.	V.S.	ABS	Waste Water Vol., cc.	Time, (Min.)	COD	T.S.	V.S.	ABS
0	111	575	91	4.88	0	0	80	587	99	0.21
23	9	668	83	0.10	250	5	17	651	101	0.14
46	-	-	-	-	500	18	-	-	-	-
65	-	-	-	-	750	50	-	-	-	-
81	33	-	-	-	1000	70	9	-	-	-
98	-	-	-	-	1250	87	-	-	-	-
116	-	-	-	-	1500	101	-	-	-	-
139	-	-	-	-	1750	119	-	-	-	-
155	18	-	-	-	2000	132	3	-	-	-
177	-	-	-	-	2250	151	-	-	-	-
192	-	-	-	-	2500	173	-	-	-	-
222	-	-	-	-	2750	191	-	-	-	-
255	33	-	-	-	3000	219	9	-	-	-
270	-	-	-	-	3250	242	-	-	-	-
287	-	-	-	-	3500	268	-	-	-	-
305	-	-	-	-	3750	279	-	-	-	-
335	107	-	-	-	4000	303	11	-	-	-
359	-	-	-	-	4250	336	-	-	-	-
378	-	-	-	-	4500	382	-	-	-	-
394	-	-	-	-	4750	403	-	-	-	-
415	17	547	60	0.63	5000	424	72	559	48	0.07
432	-	-	-	-	5250	456	-	-	-	-
452	33	-	-	-	5500	476	3	-	-	-
471	-	-	-	-	5750	495	-	-	-	-
506	-	-	-	-	6000	517	-	-	-	-
533	-	-	-	-	6250	533	-	-	-	-
560	-	-	-	-	6500	566	-	-	-	-
583	-	-	-	-	6750	586	-	-	-	-
605	486	-	-	-	7000	601	142	-	-	-
633	-	-	-	-	7250	626	-	-	-	-
648	118	523	64	0.03	7500	654	18	499	56	0.03
688	-	-	-	-	7750	684	-	-	-	-
713	94	-	-	-	8000	712	86	-	-	-
728	-	-	-	-	8250	742	-	-	-	-
756	-	-	-	-	8500	770	-	-	-	-
791	-	-	-	-	8750	797	-	-	-	-
818	102	-	-	-	9000	826	86	-	-	-
832	-	-	-	-	9250	865	-	-	-	-
848	-	-	-	-	9500	898	-	-	-	-
870	-	-	-	-	9750	928	-	-	-	-
899	86	-	-	-	10000	960	86	-	-	-

75°F., Secondary Effluent

Pittsburgh Activated Carbon, Type RB Pulverized
Surface Area = 1408 $m^2/g.$
Pore Volume = 0.79 cc./g.
Pore Radius = 11 Å

Foam Fractionation Conditions: 1200 cc. Sec. Effluent
75°F., 2" Diameter Column
Fine Gas Disperser, 15 Min.
Air Flow Rate: 66.4 x 10^{-3} CF/Min. (STP)

Analysis of Spent Carbon	--Run No.-- 13A	14A
Wt.% Sulfur	0.65	0.73
Wt.% Nitrogen	0.13	0.14

Appendix Table 32

ADSORPTION ON ACTIVATED CARBON

	15A	16A
Run No.:		
Feed Pretreatment:	Filtered	Filtered and Foamed (Using Air)
Activated Carbon:	33.7 g. (100 cc.) (Cl = 80 ppm)	34.4 g. (100 cc.) (Cl = 80 ppm)

Time (Min.)	V/V/Hr.	COD	T.S.	V.S.	ABS	Waste Water Vol., cc.	Time, (Min.)	V/V/Hr.	COD	T.S.	V.S.	ABS
0	0	76	455	80	-	0	0	0	36	459	75	0.53
28	5.4	157				250	26	5.8	44			
58	-	-				500	52	-	-			
84	5.8	64				750	79	5.6	9			
110	-	-				1000	101	-	-			
124	10.7	83			0.04	1250	123	6.8	42			0.03
141	-	-				1500	145	-	-			
154	11.5	75				1750	166	7.1	14			
167	-	-				2000	184	-	-			
177	15.0	72				2250	198	10.7	(-6)			
190	-	-	446	58	0.04	2500	212	-	-	437	70	0.02
203	11.5	68				2750	232	7.5	410			
228	-	-				3000	247	-	-			
252	6.3	56				3250	259	12.5	32			
266	-	-				3500	274	-	-			
280	10.7	5			0.03	3750	290	9.4	54			0.08
300	-	-				4000	304	-	-			
317	8.8	72				4250	320	9.4	26			
328	-	-				4500	336	-	-			
343	-	-				4750	352	-	-			
361	8.3	17	442	54	0.08	5000	360	18.8	18	433	53	0.03
385	-	-				5250	385	-	-			
413	5.4	43				5500	415	5.0	10	442	65	
435	-	-				5750	430	-	-			
472	5.6	-58				6000	451	7.1	10			
499	-	-			0.05	6250	483	-	-			0.13
533	4.4	20				6500	510	5.6	10			
555	-	-				6750	531	-	-			
584	5.2	1				7000	550	7.9	10			
616	-	-				7250	575					
641	6.0	46	431	41	0.06	7500	602	5.6	26			0.03
662	-	-				7750	627	-	-			
680	8.3	5				8000	643	9.4	20			
717	-	-				8250	659	-	-			
735	8.3	18				8500	677	8.3	18			
755	-	-			0.05	8750	700	-	-			0.12
784	5.2	5				9000	715	10.0	26			
810	-	-				9250	733	-	-			
824	10.7	-10				9500	790	2.5	10			
852	-	-				9750	820	-	-			
882	5.0	-3	416	53	0.07	10,000	850	5.0	(-14)	473	60	0.08

75°F., Secondary Effluent
Pittsburgh Activated Carbon, Type RB Pulverized
Surface Area = 1408 $m^2/g.$
Pore Volume = 0.79 cc./g.
Pore Radius = 11 Å
Foam Fractionation Conditions:
1200 cc. Sec. Effluent
75°F., 2" Diameter Column
Fine Gas Disperser, 10 Min.
Air Flow Rate: 66.4×10^{-3} CF/Min. (STP)

Appendix Table 33

ADSORPTION ON ACTIVATED CARBON

Run No.:	17A						18A					
Feed Pretreatment:	Filtered						Filtered and Foamed (Using N_2)					
Activated Carbon:	36.7 g. (100 cc.) (Cl = 100 ppm)						36.7 g. (100 cc.) (Cl = 100 ppm)					
Time (Min.)	V/V/Hr.	COD	T.S.	V.S.	ABS	Waste Water Vol. cc.	Time (Min.)	V/V/Hr.	COD	T.S.	V.S.	ABS
0	0	65	497	89	5.7	0	0	0	46	474	84	0.78
35	4.3	17				250	30	5.0	2			
60	6.0	-				500	60	5.0	-			
80	7.5	21				750	80	7.5	18			
106	5.8	-				1000	104	6.3	-			
127	7.1	17			0.13	1250	124	7.5	34			< 0.08
142	10.0	-				1500	143	7.9	-			
159	8.8	17				1750	162	7.9	18			
176	8.8	-				2000	178	9.4	-			
190	10.7	21				2250	198	7.5	18			
220	5.0	-	465	64	<0.08	2500	212	10.7	-	453	67	<0.08
240	7.5	17				2750	222	15.0	26			
254	10.7	-				3000	239	8.8	-			
271	8.8	17				3250	270	4.8	38			
282	13.6	-				3500	299	5.2	-			
297	10.0	17	-	-	0.06	3750	347	3.1	(-23)			< 0.08
308	13.6	-				4000	377	5.0	-			
322	10.7	17				4250	402	6.0	(-23)			
339	8.8	-				4500	422	7.5				
354	10.0	-				4750	440	8.3	-			
372	8.3	25	455	56	<0.08	5000	457	8.8	2	432	58	< 0.08
387	10.0	-				5250	469	12.5	-			
417	5.0	17				5500	479	15.0	34			
450	4.5	-				5750	486	21.4	-			
476	5.8	21				6000	501	10.0	26			
496	7.5	-	-	-	0.08	6250	517	9.4	-			< 0.08
522	5.8	13				6500	539	6.8	22			
550	5.4	-				6750	563	6.3	-			
578	5.4	13				7000	591	5.4	25			
592	10.7	-				7250	626	4.3	-			
614	6.8	1	444	36	0.05	7500	667	3.7	17	430	57	<0.08
644	5.0	-				7750	717	3.0	-			
672	5.4	5				8000	772	2.7	2			
714	3.6	-				8250	832	2.5	-			
759	3.3	13				8500	878	3.3	26			
795	4.2	-	-	-	0.04	8750	992	1.3	-			<0.08
843	3.1	9				9000	1112	1.3	13			
874	4.8	-				9250	-	-	-			
907	4.5	1				9500	-	-	-			
945	3.9	-				9750	-	-	-			
975	5.0	5	430	61	0.06	10,000	-	-	-			

75°F., Secondary Effluent
Pittsburgh Activated Carbon, Type RB Pulverized
Surface Area = 1408 $m^2/g.$
Pore Volume = 0.79 cc./g.
Pore Radius = 11 Å
Foam Fractionation Conditions:
1200 cc. Sec. Effluent
75°F., 2" Diameter Column
Fine Gas Disperser, 10 Min.
Nitrogen Flow Rate: 66.4 x 10^{-3} CF/Min. (STP)

Appendix Table 34

ADSORPTION ON ACTIVATED CARBON

Run No.:	19A	20A
Feed Pretreatment:	Filtered	Filtered & Foamed (Using Air)
Activated Carbon:	127g (300 cc)	127g (300 cc)

Time (Min.)	COD, ppm	Waste Water Vol., cc	COD, ppm
0	192 (Feed)	0	146 (Feed)
30	34	1000	-21
60		2000	
90	70	3000	19
125		4000	
155	27	5000	42
185		6000	
215		7000	
245		8000	
275		9000	
305	66	10,000	42
335		11,000	
365	82	12,000	50
395		13,000	
425		14,000	
455	70	15,000	46
485		16,000	
515		17,000	
545	58	18,000	11
575		19,000	
605	46	20,000	(-5)
635		21,000	
665	37	22,000	45
695		23,000	
725		24,000	
755	56	25,000	37
785		26,000	
815	45	27,000	56
845		28,000	
875		29,000	
905	33	30,000	29

Filtered Secondary Effluent: Cl = 300 ppm, T.S. = 854, V.S. = 126, ABS = 3.16, pH = 7.3
After Foaming, ABS = 0.74 ppm
Foam Fractionation Conditions: 4" diameter column, 75°F.
Fine Gas Disperser, 5 Min. Residence Time,
Continuous Operation. Air Flow Rate = 108×10^{-3} SCF/Min.
Activated Carbon: Mesh size 12 x 40, Pittsburgh Granular Activated Carbon, Type CAL (Pittsburgh Coke & Chemical Company)

Appendix Table 35

EMULSION FRACTIONATION OF WASTE WATER

Vol.% Waste Water	Solvent	Emulsion Stability,* Sec.
0	Toluene	5
25	"	15
50	"	14
75	"	15
100	"	50
0	n-Heptane	10
25	"	35
50	"	90
75	"	90
100	"	15
0	Decahydronaphthalene	25
25	"	50
50	"	110
75	"	105
100	"	120
0	Hexene-1	45
25	"	205
50	"	20
75	"	15
100	"	10
0	Nitrobenzene	450
25	"	120
50	"	15
75	"	35
100	"	35
0	Benzene	-
25	"	20
50	"	27
75	"	35
100	"	43

* 25 cc. water phase shaken for 30 sec. with 25 cc. hydrocarbon solvent.
Waste water diluted with distilled water. 76°F.
Filtered secondary effluent COD = 80-90 (estimated value).

Appendix Table 36

DIMENSIONS OF FOAM FRACTIONATION COLUMNS

Case No.	Waste Water gpm	Waste Water gpd	Column Volume For Liq., $ft.^3$(1)	Expanded Volume of Liq. (1) x 1.15 = x	Total Vol. Of Column (x) x 2	Dimensions of Foam Column, Diameter Ø, and Height, in ft.	Dimensions of Foam Receiver, Diameter Ø, and Height, in ft.
I	75	108×10^3	30	34.5	69	3Ø x 9.7	3 x 3
II	750	1.08×10^6	300	345	690	6Ø x 24	6 x 6
III	7.5×10^3	10.8×10^6	3,000	3,450	6,900	1 (16Ø x 36)	16 x 12
IV	37.5×10^3	54×10^6	15,000	17,250	34,500	6 (15Ø x 36)	21 x 15
V	75×10^3	108×10^6	30,000	34,500	69,000	11 (15Ø x 36)	21 x 15

Appendix Table 37

REQUIREMENTS OF AIR, COMPRESSOR HORSEPOWER AND HEAT LOAD TO BE REMOVED FROM COMPRESSOR

Case No.	Waste Water gpm	Waste Water gpd	Air Flow Rate MM SCF/Day	Air Flow Rate SCF/Min.	Comp. Ratio = 2/1 Air @ 30 psig HP	Heat Load To Be Removed BTU/Day
I	75	108×10^3	0.087	60	4.12	3.86×10^5
II	750	1.08×10^6	0.87	600	41.2	3.86×10^6
III	7.5×10^3	10.8×10^6	8.7	6,000	412	3.86×10^7
IV	37.5×10^3	54×10^6	43.5	30,000	2,060	1.93×10^8
V	75×10^3	108×10^6	87	60,000	4,120	3.86×10^8

Appendix Table 38

CAPITAL AND OPERATING COST OF FOAM FRACTIONATION COLUMNS

Case No.	I	II	III	IV	IV A[b]	V	V A[b]
Plant Capacity Millions, Gals.	0.108	1.08	10.8	54	54	108	108
Capital Cost, $	50,000	100,000[d]	200,000	825,000	950,000	1,400,000	1,625,000
			Operating Cost, $/Day[a]				
1. Power, $0.007/KWH	1.67	12.08	108.8	484	640	968	1,282.0
2. Supplies and Maintenance Materials. 0.5% I	0.76	1.35	3.03	12.50	14.39	21.21	24.62
3. Operating Labor, $2.00/Hr.	48.00	48.00	48.00	96.00	96.00	144.00	144.00
4. Maintenance Labor 0.5%(I)	0.76	1.35	3.03	12.50	14.39	21.21	24.62
5. Payroll Extras 0.15 (3 + 4)	7.3	7.4	7.6	16.3	16.5	24.7	25.3
6 Overhead 1.0 (3 + 4 + 5)[c]	56.06	56.75	58.63	124.80	126.89	189.91	193.92
7. Amortization 7.4% I	11.21	21.97	44.84	185.00	213.00	313.91	364.38
8. Taxes And Insurance - 1% I	1.5	1.96	6.06	25.00	28.8	42.4	49.24
9. Interest On Working Capital 0.00725 (1 thru 8)	0.82	0.99	1.91	6.63	8.01	12.03	14.77
10. Total	114.18	138.18	265.19	920.89	1,113.89	1,671.70	2,052.69
11. Operating Cost, ¢/1000 Gal.	105.72	12.79	2.47	1.71	2.06	1.55	1.90
12. 25% Return On Invest. after 25% Taxes	78.0	15.0	3.11	2.55	2.96	2.18	2.53
13. Total Cost = Operating Cost + Return On Investment	183.7	27.8	5.6	4.3	5.0	3.7	4.4

(a) Based on 330 days per year operation.
(b) Alternate Compressor
(c) OSW uses 30% overhead on labor, here 100% was used.
(d) Operating cost calculated on 98,000.

Appendix Table 39-a

FOAM FRACTIONATION COST SUMMARY

Item	Case I (75 gpm)	Case II (750 gpm)	Case III (7,500 gpm)	Case IV (37,500 gpm)	Case IV A (37,500 gpm)	Case V (75,000 gpm)	Case V A (75,000 gpm)
Pumps	7,700	13,200	50,800	166,500	166,500	332,000	332,000
Compressors	8,500	24,000	22,300	261,800	361,800	413,000	579,000
Foam Column	2,200	6,200	12,100	69,700	69,700	127,000	127,000
Foam Collapsing Chambers	1,600	3,500	20,900	73,700	73,700	150,000	150,000
Total Direct Material and Labor	20,000	46,900	106,100	571,700	671,000	1,022,000	1,188,000
Contractor's Indirect Costs	24,000	40,000	69,000	160,000	182,000	240,000	270,000
Contract Cost	44,000	86,900	175,100	731,700	853,700	1,262,000	1,458,000
Contingency	4,400	8,700	17,500	73,200	85,400	126,000	146,000
Total Cost	48,400	95,600	192,600	804,900	939,100	1,388,000	1,604,000
Call	$50,000	$100,000	$200,000	$825,000	$950,000	$1,400,000	$1,625,000

Costs in Dollars

1. The estimates are based on detailed engineering, procurement and erection by a contractor.
2. Estimates cover battery limits facilities only and exclude the following:
   a) Offsite feed lines
   b) Effluent lines
   c) Power supply to site and transformation to required voltages
   d) Land cost
   e) Site preparation
3. Costs are present day West Coast (U.S.A.)
4. Cost differential between cases IV and IV A and V and V A reflects alternate compressor sizes, all other equipment remaing the same.
5. All foam columns were estimated as vertical tanks with a pad foundation.
6. All foam collapsing chambers were estimated as supported by structural steel frames.
7. Contractor's field overheads include temporary construction, field supervision, payroll burden, and tools and equipment.
8. No allowance has been included for basic design specifications.

Appendix Table 39-b

FOAM FRACTIONATION CASE I - 75 pgm

	Direct Material And Labor
Pumps with Drivers	
2 req'd.; ΔP - 40 psi 75 gpm; horiz. centrifugal Electric drive hP = 5	7,700
Compressor with Driver	
1 req'd.; reciprocating; electric drive; 60 SCF/Min. comp. ratio = 2:1	8,500
Foam Columns	
1 req'd.; carbon steel; 3' dia. x 10'; vertical	2,200
Foam Collapsing Chambers	
1 req'd.; 3' dia. x 3'; carbon steel 12 ft. support structure	1,600
Total Direct M & L	$20,000
Contractor's Field Overheads, Engineering and Fees	24,000
Contract Cost	$44,000
Contingency	4,400
Total Cost	$48,400
Call	$50,000

Appendix Table 39-c

FOAM FRACTIONATION CASE II - 750 gpm

	Direct Material And Labor
Pumps with Drivers	
2 req'd.; ΔP = 40 psi; 750 gpm; horiz. centrifugal electric drive hp = 30	13,200
Compressor with Driver	
1 req'd.; reciprocating; electric drive; 600 SCF/Min. comp. ratio = 2:1	24,000
Foam Column	
1 req'd.; carbon steel; 6' dia. x 24'; vertical	6,200
Foam Collapsing Chamber	
1 req'd.; 6' dia. x 6' carbon steel; 25' support structure	3,500
Total Direct M & L	$46,900
Contractor's Field Overheads Engineering and Fees	40,000
Contract Cost	$86,900
Contingency	8,700
Total Cost	$95,600
Call	$100,000

Appendix Table 39-d

FOAM FRACTIONATION CASE III - 7,500 gpm

	Direct Material And Labor
Pumps with Drivers	
2 req'd.; ΔP = 40 psi 7500 gpm; horiz. centrifugal electric drive hp = 250	50,800
Compressor with Driver	
1 req'd.; rotary; electric drive; 6000 SCF/Min. comp. ratio = 2:1	22,300
Foam Column	
1 req'd.; carbon steel; 16' dia. x 36'; vertical	12,100
Foam Collapsing Chamber	
1 req'd.; 16' dia. x 12' carbon steel; 36' support structure	20,900
Total Direct M & L	$106,100
Contractor's Field Overheads, Engineering and Fees	69,000
Contract Cost	$175,100
Contingency	17,500
Total Cost	$192,600
Call	$200,000

Appendix Table 39-e

FOAM FRACTIONATION CASE IV - 37,500 gpm

	Direct Material And Labor
Pumps with Drivers	
2 req'd.; ΔP = 40 psi 37,500 gpm; horiz. centrifugal electrical drive hp = 1000	166,500
Compressor with Driver	
1 req'd.; centrifugal; electric drive; 30,000 SCF/Min. comp. ratio = 2:1	261,800
Foam Columns	
6 req'd.; carbon steel 15' dia. x 36'; vertical	69,700
Foam Collapsing Chambers	
3 req'd.; 21' dia. x 15' carbon steel; 36' support structure	73,700
Total Direct M & L	$571,700
Contractor's Field Overheads, Engineering and Fees	$160,000
Contract Cost	$731,700
Contingency	73,200
Total Cost	$804,900
Call	$825,000

Appendix Table 39-f

FOAM FRACTIONATION CASE IV A - 37,500 gpm

	Direct Material And Labor
Pumps with Drivers	
2 req'd.; ΔP = 40 psi 37,500 gpm; horiz. centrifugal electric drive hp = 1000	166,500
Compressor with Driver	
1 req'd.; centrifugal' electric drive; 30,000 SCF/Min. comp. ratio = 3:1	361,800
Foam Columns	
6 req'd.; carbon steel 15' dia. x 36'; vertical	69,700
Foam Collapsing Chambers	
3 req'd.; 21' dia. x 15' carbon steel; 36' support structure	73,700
Total Direct M & L	$671,700
Contractor's Field Overheads, Engineering and Fees	182,000
Contract Cost	$853,700
Contingency	85,400
Total Cost	$939,100
Call	$950,000

Appendix Table 39-g

FOAM FRACTIONATION CASE V - 75,000 gpm

	Direct Material And Labor
Pumps with Drivers	
4 req'd.; ΔP = 40 psi 37,500 gpm; horiz. centrifugal electric drive hp = 1000	332,000
Compressor with Driver	
1 req'd.; centrifugal; electric drive; 60,000 SCF/Min. comp. ratio = 2:1	413,000
Foam Columns	
11 req'd.; carbon steel; 15' dia. x 36'; vertical	127,000
Foam Collapsing Chambers	
6 req'd.; 21' dia. x 15'; carbon steel; 36' support structure	150,000
Total Direct M & L	$1,022,000
Contractor's Field Overheads, Engineering and Fees	240,000
Contract Cost	$1,262,000
Contingency	126,000
Total Cost	$1,388,000
Call	$1,400,000

Appendix Table 39-h

FOAM FRACTIONATION CASE V A - 75,000 gpm

	Direct Material And Labor
Pumps with Drivers	
4 req'd.; ΔP = 40 psi 37,500 gpm; horiz. centrifugal electric drive hp = 1000	332,000
Compressor with Driver	
1 req'd.; centrifugal; electric drive; 60,000 SCF/Min. comp. ratio = 3:1	579,000
Foam Columns	
11 req'd.; carbon steel; 15' dia. x 36'; vertical	127,000
Foam Collapsing Chambers	
6 req'd.; 21' dia. x 15' carbon steel; 36' support structure	150,000
Total Direct M & L	$1,188,000
Contractor's Field Overheads, Engineering and Fees	270,000
Contract Cost	$1,458,000
Contingency	146,000
Total Cost	$1,604,000
Call	$1,625,000

Appendix Table 40

ALTERING pH OF WASTE WATER

Waste Water Batch No.	Initial pH	Final pH	Milliequivalents/Liter of HCl or NaOH to Alter pH
26	6.7	5.7	1.89
26	6.7	4.7	2.64
26	7.2	8.2	0.60
26	7.2	9.2	1.33
27	7.1	6.1	1.59
27	7.1	5.1	2.65
27	7.1	8.1	0.56
27	7.1	9.1	1.42
28	7.1	6.1	1.69
28	7.1	5.1	2.74
28	7.1	8.1	0.51
28	7.1	9.1	1.46

Filtered Secondary Effluent Titrated with 0.100 N HCl and 0.1015 N NaOH.

Waste Water from Little Ferry, New Jersey

	ppm				
Batch No.	COD	ABS	CI	T.S.	V.S.
26	54	2.84	70	410	75
27	94	-	80	455	80
28	87	5.70	100	497	89

Appendix Table 41

METALS CONTENT OF SECONDARY EFFLUENT

Feed - Secondary Effluent Treatment	Filtered	Filtered and Foamed*
Analyses, ppm		
COD	131.8	120.2
T.S.	506	519
V.S.	80	90
Cl	130	130
ABS	4.22	0.31
Metals Content, ppm		
Na	75	74
Ca	44	46
Mg	11	11
V	< 4.6	< 4.6
Si	6.1	7.8
Al	< 0.9	< 0.9
Fe	< 0.4	< 0.4
Ni	< 0.4	< 0.4
Mn,K,Sr,Cu,Cr,B	Trace	Trace

* Experimental Conditions:

1200 cc. Filtered Secondary Effluent (Bergen County Sewage Authority)
75°F., 15 Min. Aeration Time
Fine Gas Disperser
66.4×10^{-3} CF/Min. (STP)
2" Diameter Column

Appendix Table 42

RATE OF RISE OF AIR BUBBLES

2" Diameter foam fractionation column.
1200 cc. of distilled water, 75°F.
68 cm. from gas disperser to top of liquid level in column.
Fine gas disperser: 4.5-5.5 microns (pore diameter).
Medium gas disperser: 10-15 microns (pore diameter).

Gas Disperser	Air Flow Rate, SCF/Min.	Pressure Before Gas Disperser, psig	Time Of Bubble Rise, sec. (a)
Medium	27×10^{-3}	5.0	4
	66.4×10^{-3} (b)	11.5	4
Fine	27×10^{-3}	5.0	3.5-4
	66.4×10^{-3} (b)	11.5	4-5

(a) Bubble rise was estimated visually and may be in error by about $\pm$ 2 seconds.
(b) Air flow rates normally used in batch foam fractionation runs.

Appendix Table 43

VARIATION OF FOAM PHASE VOLUME

Run No.	Foam Overhead, cc.	Deviation	(Deviation)^2
1	26	-3	9
2	22	+1	1
3	27	-4	16
4	20	+3	9
5	32	-9	81
6	14	+9	81
7	24	-1	1
8	14	+9	81
9	26	-3	9
10	24	-1	1
11	28	-5	25
Sum	257	48	314

Mean = 23 cc. (Batch 27)

Standard Deviation = $\sqrt{\frac{314}{10} = 31.4}$ = 5.6 cc.

Run No.	Foam Overhead, cc.	Deviation	(Deviation)^2
1	34	-3	9
2	28	+3	9
3	32	-1	1
4	42	-11	121
5	32	-1	1
6	32	-1	1
7	32	-1	1
8	28	+3	9
9	28	+3	9
10	26	+5	25
11	32	-1	1
Sum	346	33	187

Mean = 31 cc. (Batch 28)

Standard Deviation = $\sqrt{\frac{187}{10} = 18.7}$ = 4.3 cc.

Experimental Conditions:

1200 cc. Filtered Secondary Effluent
Fine Gas Disperser
2" Diameter Column
75°F., 10 Min. Aeration Time
66.4 x 10^{-3} SCF/Min.

Appendix Table 44

VARIATION OF FOAM PHASE VOLUME

Run No.	Foam Overhead, cc.	Deviation	(Deviation)^2
1	160	+29	841
2	165	+24	576
3	185	+ 4	16
4	190	- 1	1
5	130	+50	2500
6	210	-21	441
7	270	-81	6561
8	160	+29	841
9	170	+19	361
10	190	- 1	1
11	260	-71	5041
12	178	+11	121
Sum	2268	341	17301

Mean = 189

Standard Deviation = $\sqrt{\frac{17301}{11}}$ = 1572.8 = 39.6

Experimental Conditions:

1200 cc. Filtered Secondary Effluent
Fine Gas Disperser
2" Diameter Column
75°F., 15 Min. Aeration Time
66.4 x 10^{-3} CF/Min. (STP)

Foam overheads were combined and 1200 cc. were foamed at same conditions as above. Results of this second foam fractionation experiment:

Foam Overhead: 720 cc., 6.67 ppm ABS
Foamed Liquid: 480 cc., 0.56 ppm ABS

Appendix Table 45

VARIATION OF COD RESULTS

Standard Sample: Tartaric Acid

No.	COD, ppm	Deviation	$(\text{Deviation})^2$
1	534.8	- 4.67	21.81
2	525.6	+ 4.53	20.52
3	512.0	+18.13	328.70
4	526.0	+ 4.13	17.06
5	532.6	- 2.47	6.10
6	533.1	- 2.97	8.82
7	534.9	- 4.77	22.75
8	520.0	+10.13	102.62
9	552.9	-22.77	518.47
10	529.4	+ 0.73	0.533
Sum	5301.3	75.30	1047.38

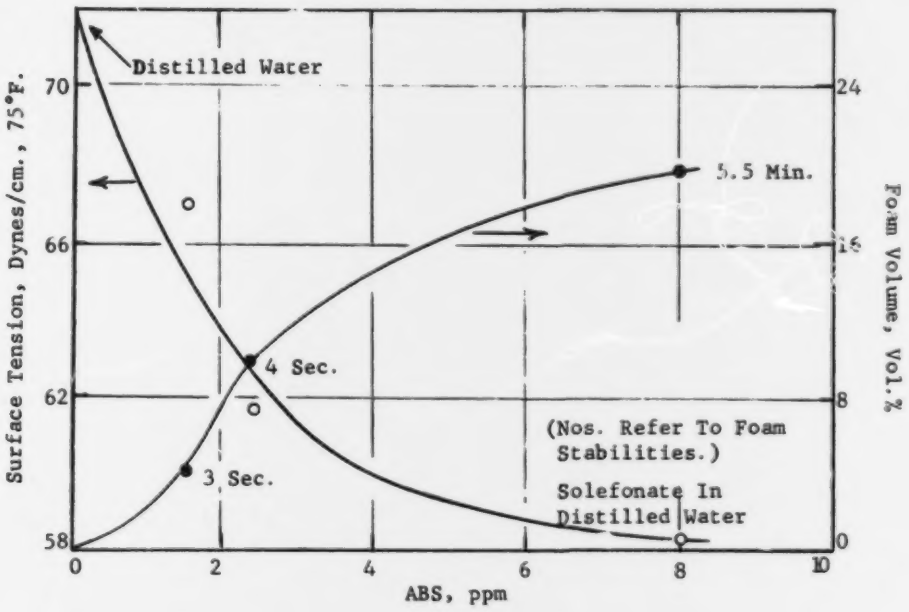
$$\text{Mean} = \frac{5301.3}{10} = 530$$

$$\text{Deviation} = (\bar{d}-d)$$

$$\text{Standard Deviation} = \sqrt{\frac{\Sigma(\bar{d}-d)^2}{N-1}} \sim 10.8$$

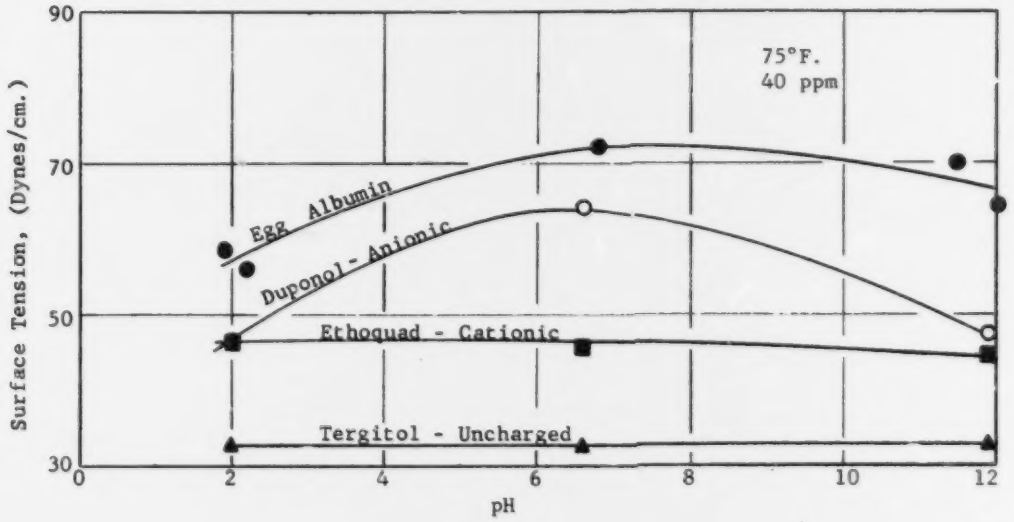
Appendix Figure 1

FOAM VOLUME INCREASES AS
SURFACE TENSION OF PURE ABS SOLUTIONS DECREASES



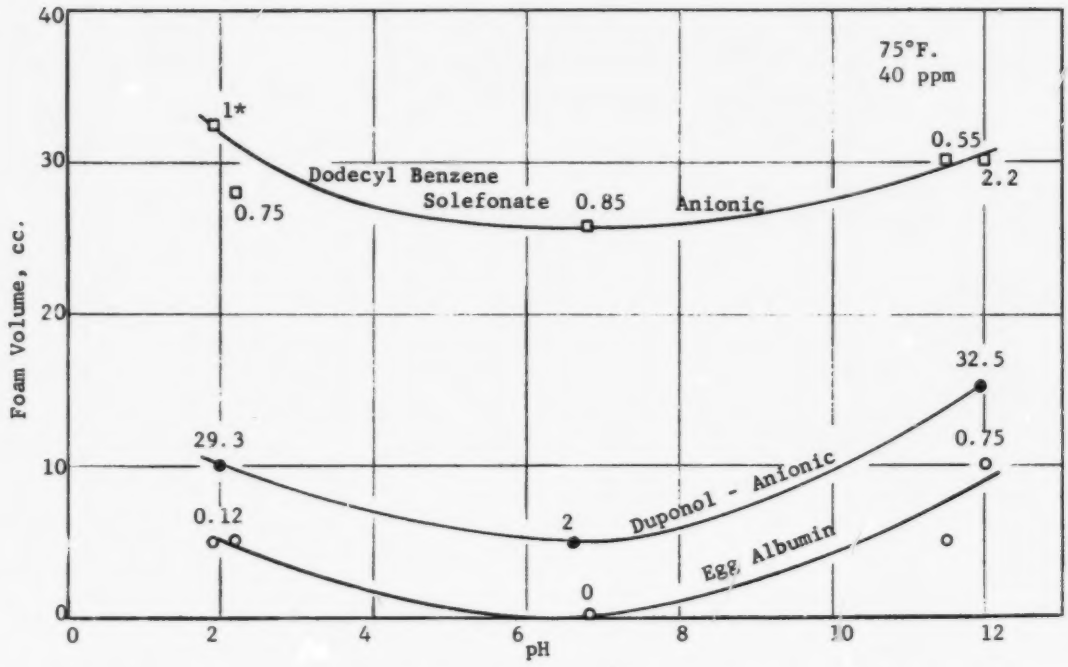
Appendix Figure 2

EFFECT OF pH ON SURFACE TENSION OF VARIOUS DETERGENT SOLUTIONS



Appendix Figure 3

EFFECT OF pH ON FOAM VOLUME AND FOAM
STABILITY OF DIFFERENT DETERGENTS AND EGG ALBUMIN

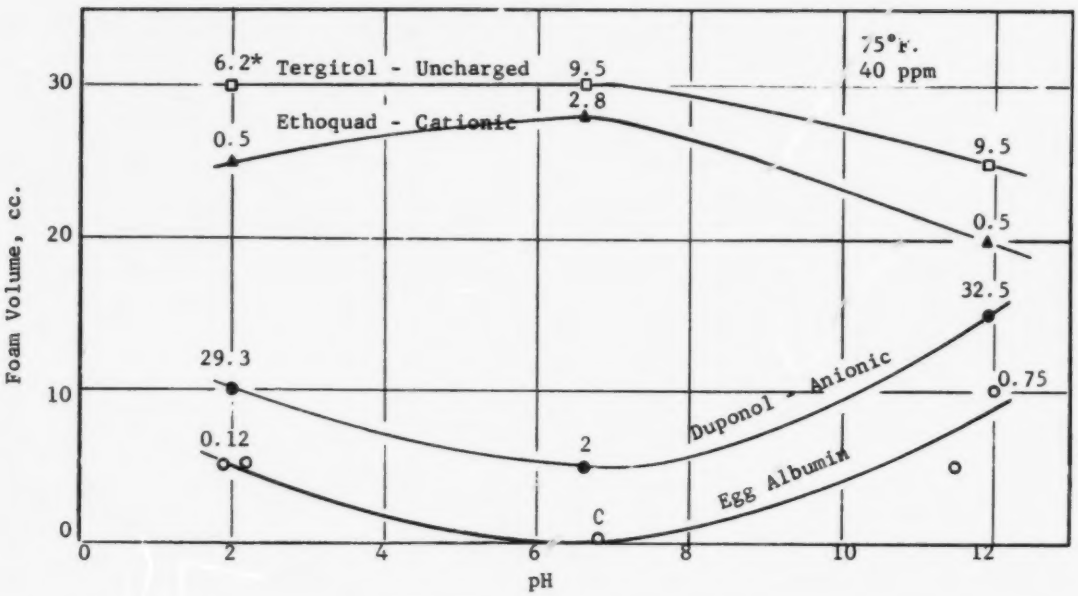


* Numbers on points indicate foam stability in hours.

Foam volume and stability measured using 50 cc of solution in a 100 cc graduated cylinder. pH altered using H_2SO_4 or NaOH.

Appendix Figure 4

EFFECT OF pH ON FOAM VOLUME AND FOAM
STABILITY OF DIFFERENT DETERGENTS AND EGG ALBUMIN

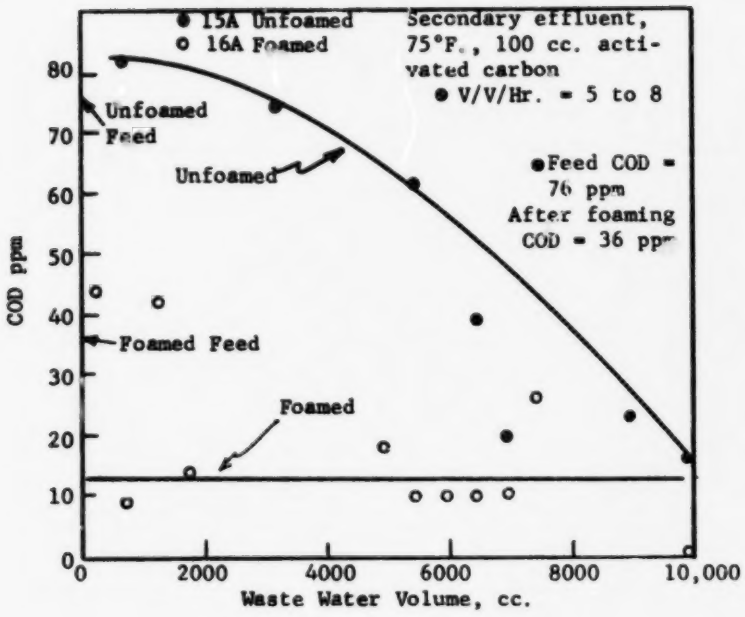


* Numbers on points indicate foam stability in hours.

Foam volume and stability measured using 50 cc of solution in a 100 cc graduated cylinder. pH altered using H_2SO_4 or NaOH.

Appendix Figure 5

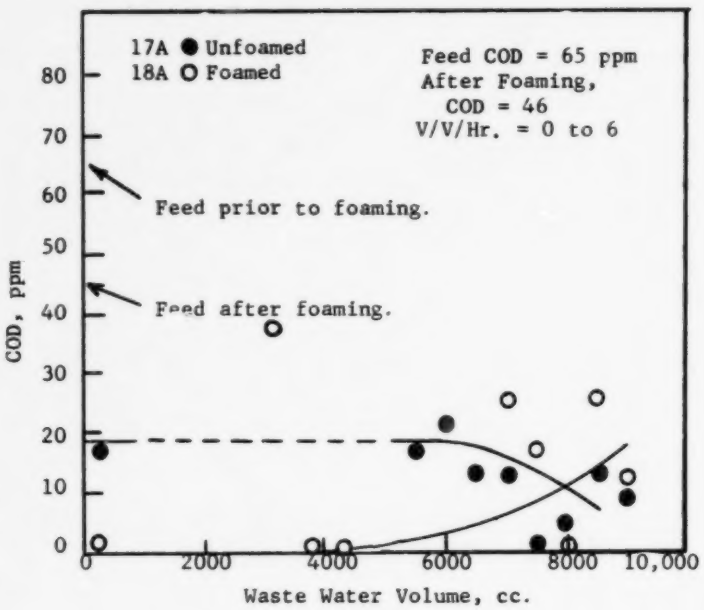
ACTIVATED CARBON USED TO
REMOVE COD MATERIALS FROM EFFLUENTS



* It is interesting to note that the COD concentration steadily decreased with more effluent passing over the activated carbon, while the COD for the foamed effluent did not change. Further work is needed.
Data corresponding to space velocities of 5 to 8 v/v/hr. only have been plotted here.

Appendix Figure 6

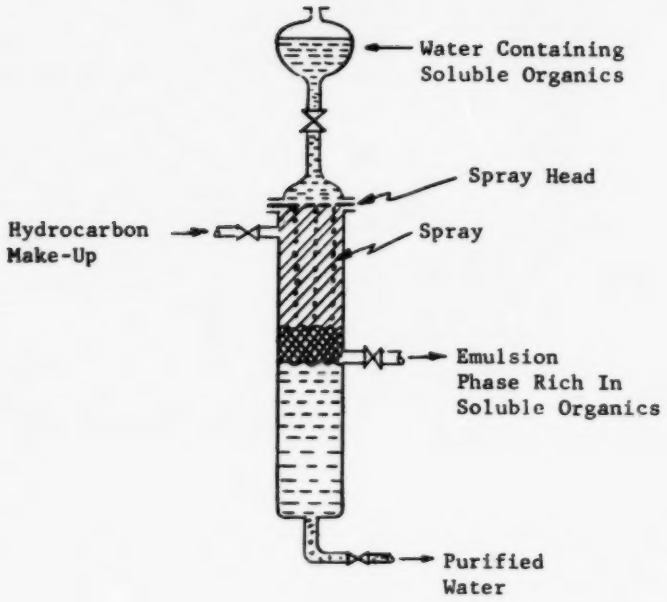
ACTIVATED CARBON USED TO
REMOVE COD MATERIALS FROM EFFLUENTS



Data corresponding to space velocities of 0 to 6 v/v/hr. only have been plotted here.

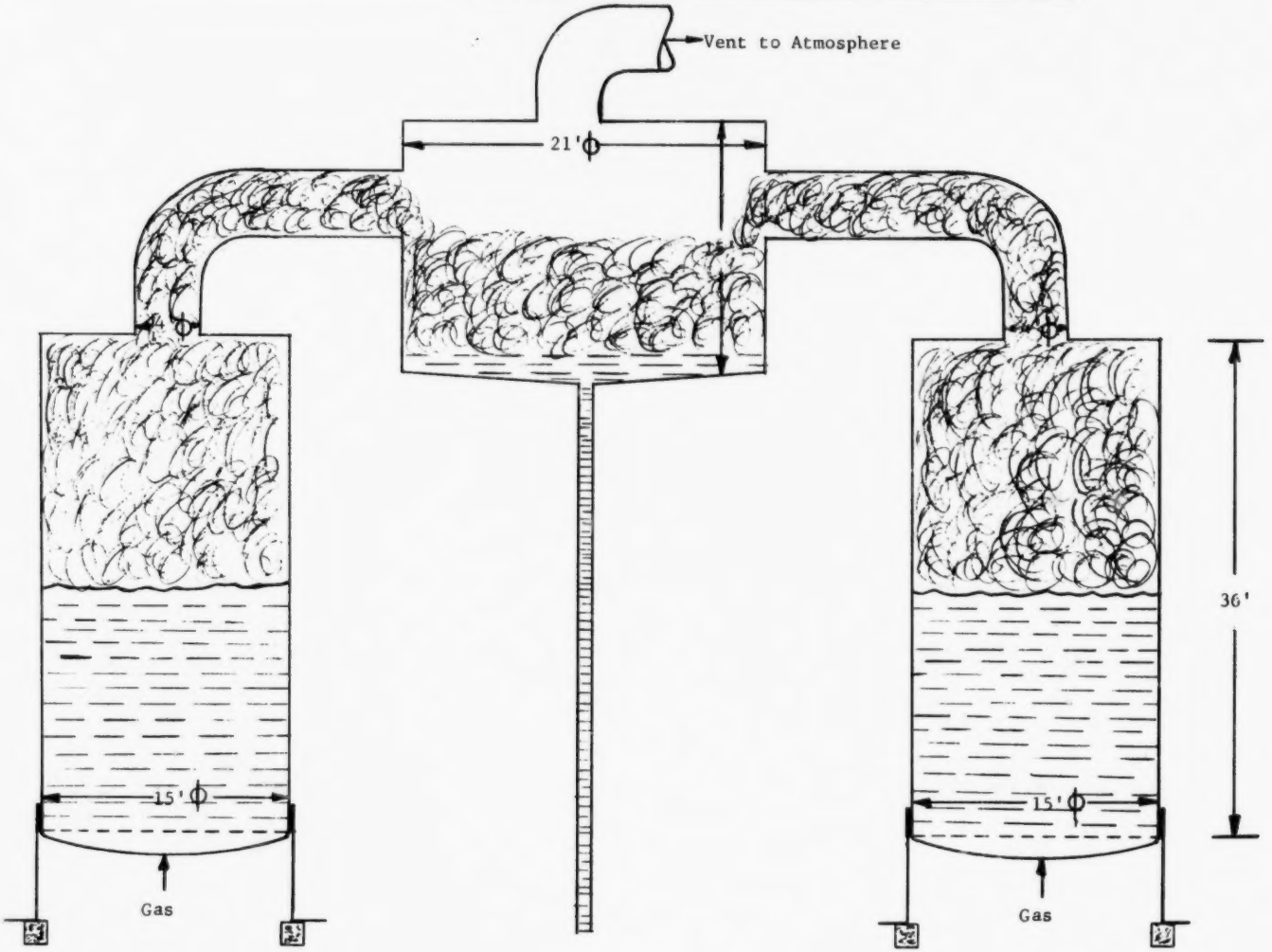
Appendix Figure 7

CONTINUOUS EMULSION FRACTIONATION UNIT



Appendix Figure 8

DESIGN OF TWO FOAM FRACTIONATION COLUMNS WITH A SINGLE FOAM RECEIVER, SIX COLUMNS CAN HANDLE 54 x 106 GAL./DAY



APPENDIX B
COMPOSITION OF DETERGENTS

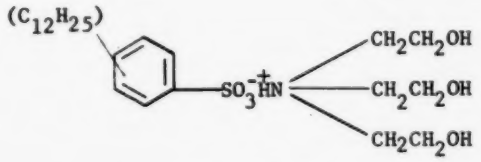
1. Duponol (WA dry) $C_{12}H_{25}\ SO_4\text{-}Na^+$

Sodium Lauryl Sulfate	44.0-49.5%
Free Fatty Alcohols	1.5-3.5%
pH	9-10

Reference: Dyes and Chemicals Bulletin, E. I. DuPont De Nemours and Co. (Inc.), Wilmington 98, Delaware, "DuPont Sodium Lauryl Sulfates."

2. Solefonate 103

This is a 60% Triethanolamine salt dodecyl benzene sulfonate.



Total Sulfonate	58.7%
Free TEA	9.2%
TEA Sulfate	3.2%
H_2O	30.0%

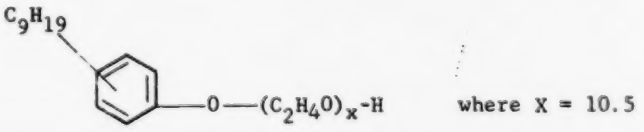
Reference: Technical Bulletin, Sole Chemical Corp., 27 East Monroe Street, Chicago 3, Illinois.

3. Tergitol Nonionic (NPX)

A nonyl phenyl polyethylene glycol ether containing 105 moles of ethylene oxide.

Active ingredient:	100%
Hydrophobe:	Nonyl phénol
Hydrophil:	10.5 moles of ethylene acid

Postulated chemical structure

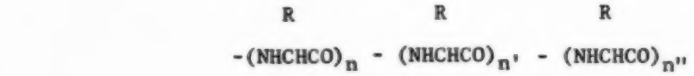


Reference: "Tergitol Sulfactants" Union Carbide Chemicals Co., 270 Park Avenue, New York 17, New York.

4. Egg Albumin

Molecular weight: 40,500 - 46,000
Isoelectric point: 4.82 - 4.90 pH units

General Structure:



Proteins may react with both acids and bases. Protein molecules usually contain charged carbonyl and basic groups in neutral solution. At the isoelectric point the dissociation of acid and basic groups is the same and the solubility of the protein in water is at a minimum.

Reference: Fieser & Fieser, "Organic Chemistry", Reinhold Publishing Corp.,N.Y.

5. Ethoquad

18/25 polyethoxy (15) stearyl methyl ammonium chloride

General Structure: $R_4N^+ Cl^-$

Reference: B. L. Karger and L. B. Rogers, Anal. Chem., 33, 1165 (1961).

APPENDIX C
EQUIPMENT

Air Rotameter: 02F 1/8 16-5/70 (Fischer-Porter) S.S. ball.

Nitrogen Rotameter: Same as above.

Feed Inlet Pump: Eastern Industries, General Electric, Type 100.

Feed Outlet Pump: Eastern Industries, General Electric, Type 209, Pump Model B-1, Serial No. COK-0216.

CENCO-DU NOUY Tensiometer: No. 70535

Rotameter for Liquids: Brooks, Tube R-6-15-B, 1/4" Float, S.S.

Welsbach T-23 Laboratory Ozonator.

Welsbach Ozone Meter, Model C.

APPENDIX D
SURFACE TENSION MEASUREMENTS

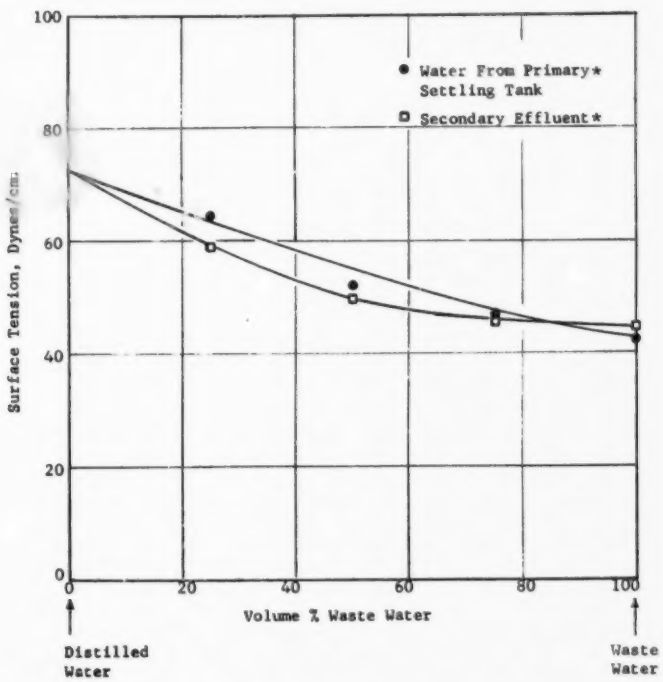
Soluble Organics In Waste Water Decrease Water Surface Tension

Surface tension measurements of waste water samples were made to help guide the foam fractionation study. Filtered waste water samples were diluted with different amounts of distilled water and the surface tension of the solutions was measured using a platinum ring tensiometer. The interfacial tension of these streams with benzene was also measured. The data indicate that soluble organics in the primary effluent and the secondary effluent are surface active because increasing concentrations of the samples in distilled water decreased its surface tension appreciably. Comparison of surface tension versus concentration of waste water for these two effluents indicates that both decrease the surface tension of distilled water by approximately identical amounts.

Interfacial tension data on two similar effluents sampled on a different day indicate that the water soluble organics are interfacially active. Figures 1, 2 and 3.

Figure 1

SURFACE TENSION OF WASTE WATER EFFLUENTS

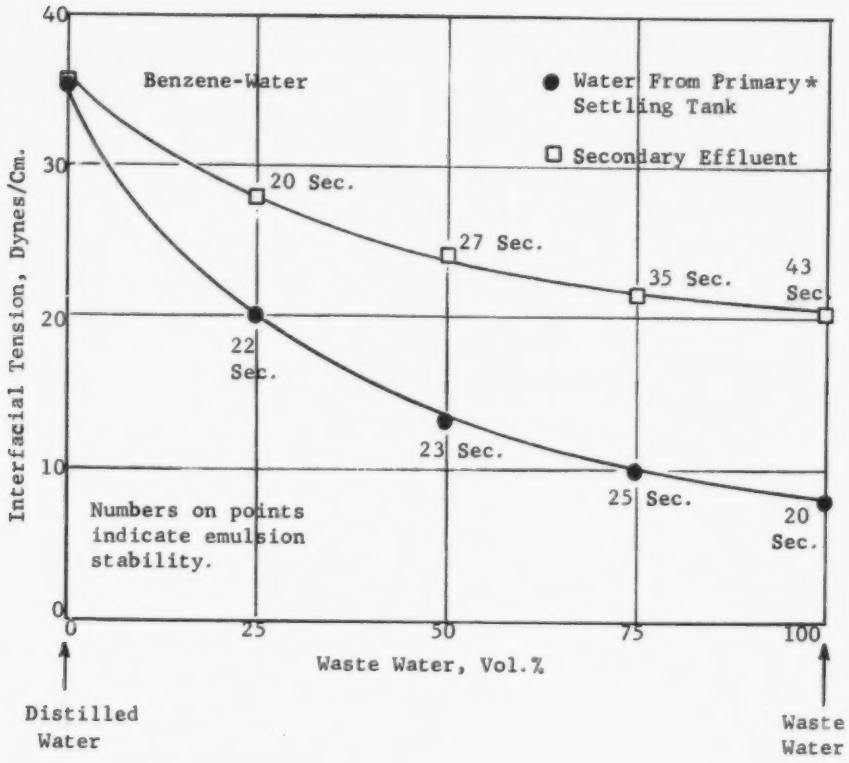


* Bergen County waste water treatment plant filtered through a Whatman #5 filter paper.

Preceding page blank

Figure 2

INTERFACIAL TENSION BETWEEN BENZENE
AND PRIMARY OR SECONDARY EFFLUENTS



* Bergen County waste water treatment plant, filtered through Whatman #5 filter paper (75°F.).

Figure 3a

CHANGES OF SURFACE TENSION AND FOAM STABILITY OF PRIMARY AND SECONDARY EFFLUENT DUE TO DILUTION WITH DISTILLED WATER AND FILTRATION OR CENTRIFUGATION

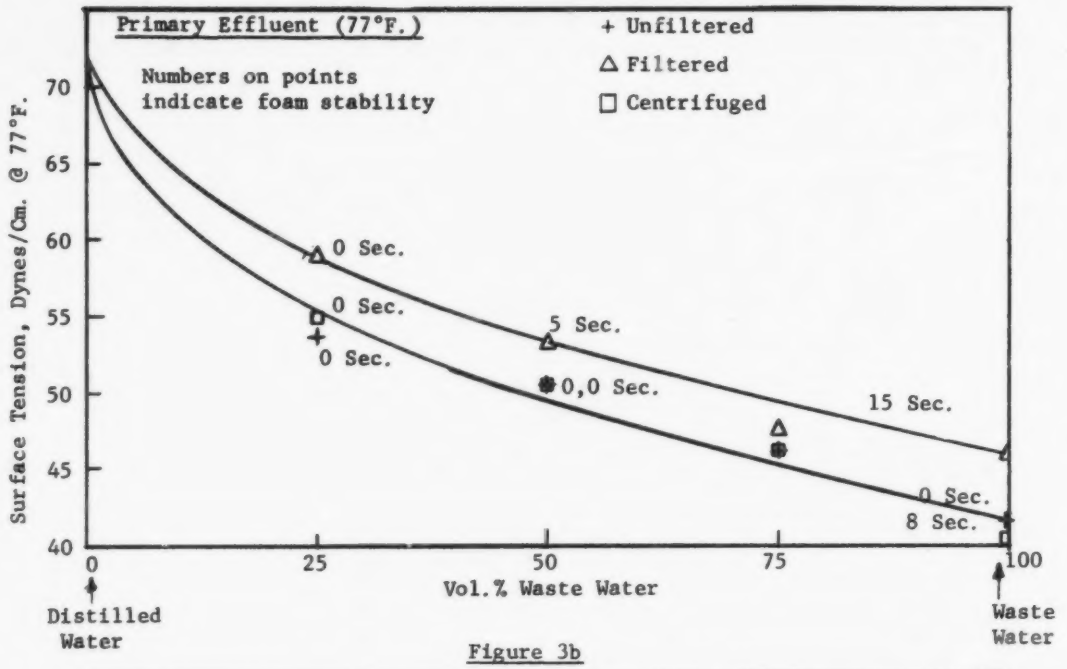
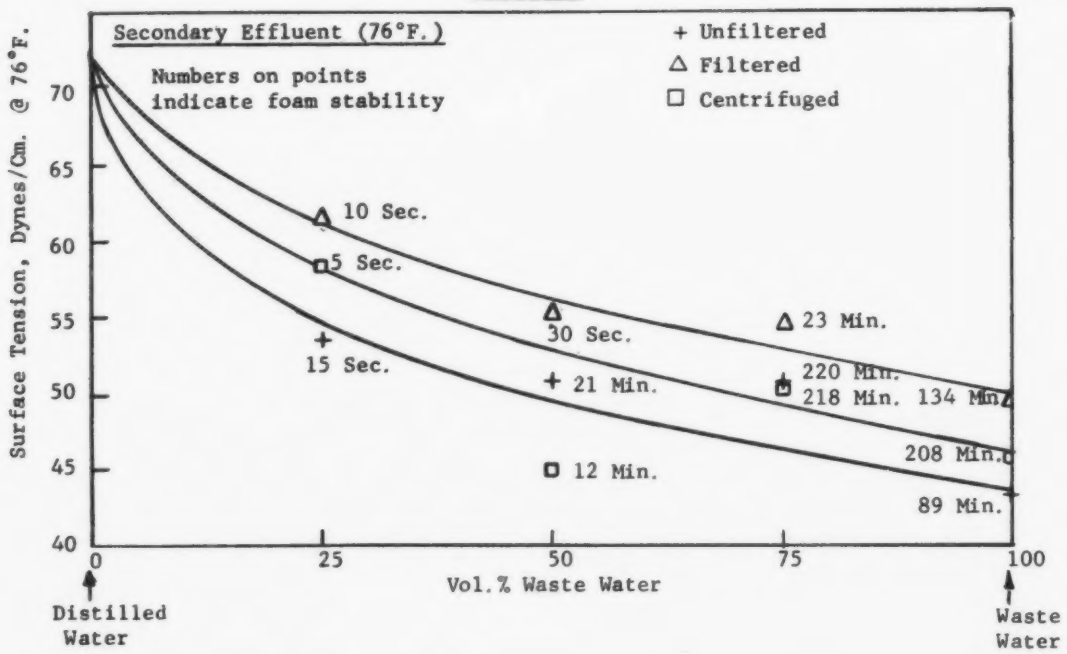


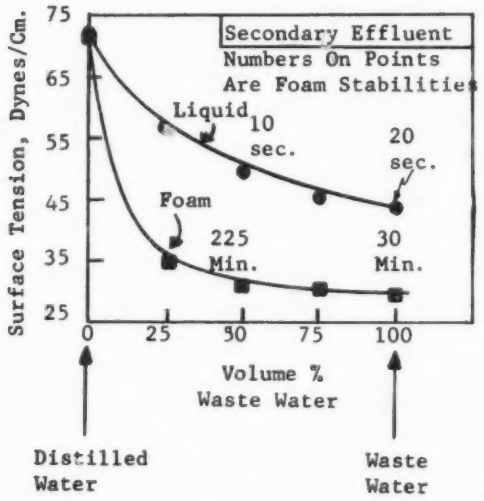
Figure 3b



In addition to taking samples of the primary and secondary effluent, samples of the foam blanket on the surface of the secondary effluent (Little Ferry, N. J.) were studied. As expected, the liquid obtained from this collapsed foam decreased the surface tension of distilled water more than secondary effluent did. This is because the foam phase contains more surface active materials than the liquid secondary effluent in contact with it. This view is supported by the high foam stability of the liquid obtained from the collapsed foam as compared to that of the secondary effluent, 30 minutes for the former vs. 20 seconds for the latter (Figure 4).

Figure 4

FOAM PHASE ON SECONDARY EFFLUENT
STREAM CONTAINED MORE WATER SOLUBLE ORGANICS



APPENDIX E
PREDICTION OF ENRICHMENT BY FOAM FRACTIONATION

Surface Activity Increases With Increased Molecular Weight

Any water-soluble organic molecule is surface active and should be amenable to removal by foam fractionation. The foam stabilities of the solutions of some of these molecules in water may, however, be so low that their removal may not be practical. Also, some molecules may lower the water surface tension to such small extents that enrichment in the foam may be very insignificant.

To relate surface activity and molecular weight, dilute solutions of methanol through n-hexanol were prepared in distilled water and surface tensions was measured for solutions containing different concentrations of the alcohols. The data indicate that the greatest surface tension decrease occurs with the high molecular weight alcohols. This substantiates the hypothesis that at least within a homologous series, surface activity increases with increase of the solute's molecular weight. That surface activity increases with increased molecular weight is related to solubility. Higher molecular weight alcohols are less soluble in water than lower molecular weight alcohols. For example, hexanol in concentrations higher than 0.55 wt.% could not be dissolved in the water (two liquid phases were formed) while 0.8 wt.% of the lower alcohols was dissolved in water.

Solubility and surface activity are related. This is because solubility results from a molecule collecting in regions of the solution where it is most surrounded by the solvent liquid, whereas surface activity results from the molecules being least surrounded. Everything being equal, maximum surface activity is obtained under conditions of minimum solubility.

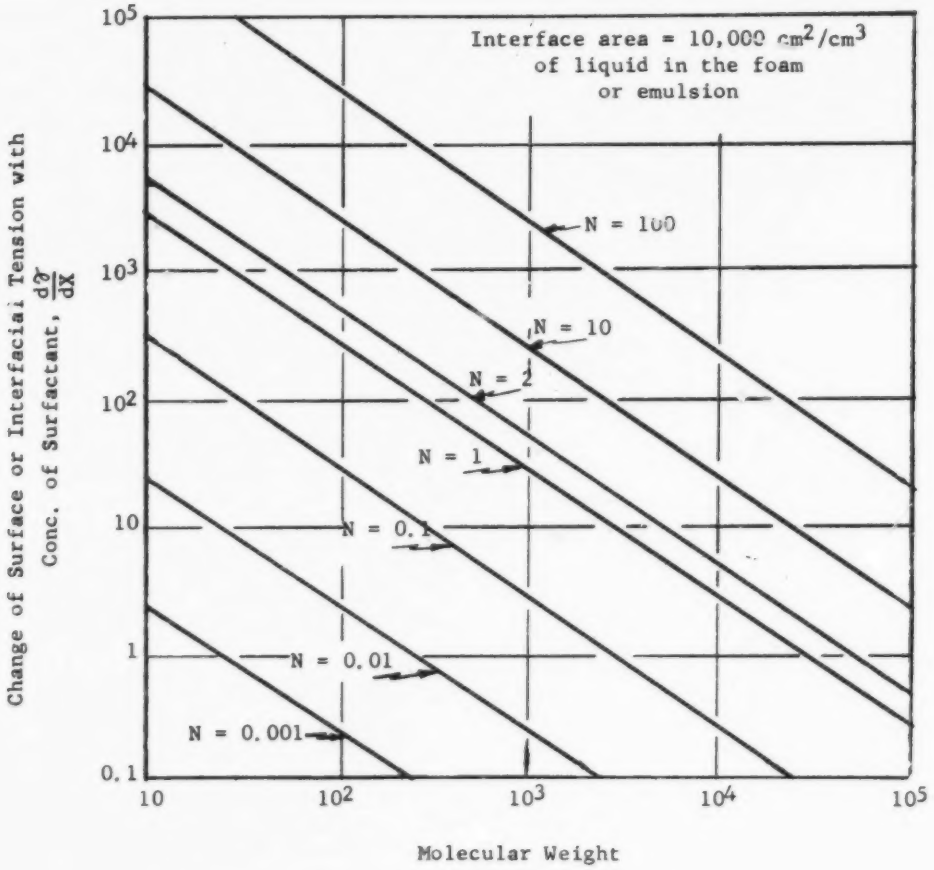
Foam stabilities of these dilute alcohol solutions were also measured as described previously. These foam stabilities are low and undoubtedly depend on more than one variable. See Figure 1 on page 146.

The surface tension concentration data did not only serve to explain the effect of molecular weight on surface activity; they can also be used to predict quantitatively the ratio of the concentration of alcohol in the foam phase to the concentration in the liquid phase in equilibrium with it. Calculations based on the Gibbs' equation show that enrichments in the foam phase increase steadily from methanol to hexanol; a sample calculation is shown below.

Feed: 0.2 wt.% alcohol in water
10,000 cm^2 of foam surface/cc. of liquid

Alcohol	Mol. Wt.	$d\gamma/dC$ Dynes/Cm./1 Wt.%	C foam/C Liq.
Methanol	32	3.7	1.006
Ethanol	46	3.7	1.006
n-Propanol	60	8.8	1.03
n-Butanol	74	17.2	1.05
n-Pentanol	88	29.5	1.09
n-Hexanol	102	120	1.70

PREDICTION OF ENRICHMENT BY FOAM FRACTIONATION



Enrichment in the foam or emulsion phase as a function of surfactant molecular weight and change of surface or interfacial tension with concentration.

Since the ease of removal of water soluble organics by foam fractionation can be increased by lowering their solubility in waste water, operating at low temperatures or at different pH conditions may be effective in enriching separations.

(For complete details, see Foam and Emulsion Fractionation, chapter in "Advances in Petroleum Chemistry and Refining", Vol. VII, by I. A. Eldib)

PREDICTED ENRICHMENTS IN FOAM PHASE AS A FUNCTION OF SURFACE ACTIVITY OF ALCOHOLS

Basic Equations

$$Y = X + 100\ AM \qquad (1)$$

$$\Gamma = \frac{X}{RT} \cdot \frac{d\sigma}{dX} \qquad (2)$$

where:

A = $cm.^2$ of surface area/$cm.^3$ of liquid in foam.

Y = solute conc. in collapsed foam, wt.%.

X = solute conc. in bulk liquid, wt.%.

Γ = surface excess, mols./$cm.^2$.

M = molecular weight.

Combining (1) and (2)

$$Y = X\left[1 - (100\ MA/8.3 \times 10^7 \times 300)\ (d\sigma/dX)\right] \qquad (3)$$

which can be simplified by writing it in the form:

$$Y = X\ (1 + N)$$

Several charts can be constructed for different interface areas expressed as $cm.^2/cm.^3$ of liquid in the foam phase. The graph attached here was constructed for 10,000 $cm.^2/cm.^3$ of interface in the foam. This chart is used as follows:

- Look up or determine the molecular weight of the active compound to be separated.
- Look up or determine the rate of change of surface tension with concentration of the active compound ($d\sigma/dX$) at the bulk liquid concentration. In the example shown here, surface tension measurements were actually carried out. The concentrations should be expressed in wt.%.
- Read N.

• Determine Y for the concentration if the relation:

$$Y = X (N + 1)$$

Example

(1) n-Pentanol Wt.% = 0.2.

(2) From γ vs. X curve $d\gamma/dX$ = 29.5 dynes/cm./wt.% at X = 0.2 wt.%.

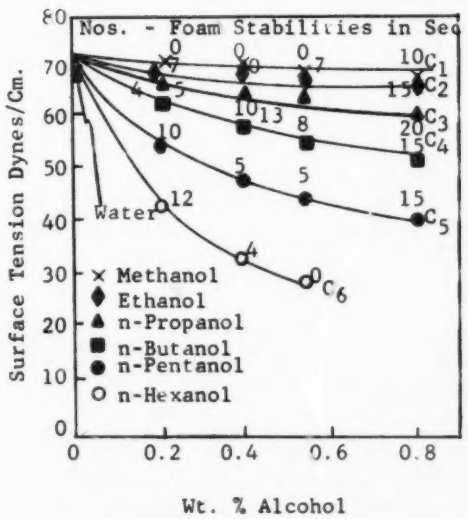
(3) Molecular weight = 88.

(4) Read N from chart: ordinate of 29.5 and abscissa of 88. Therefore, N = 0.09.

(5) Therefore, $\frac{Y}{X} = N + 1 = 0.09 + 1 = 1.09$ and $\frac{Y}{X}$ = conc. surfactants in foam/conc. surfactants in liquid.

Figure 1

SURFACE TENSION OF ALCOHOL SOLUTIONS



APPENDIX F
FOAM FRACTIONATION OF BARSTOW EFFLUENT
(SANTE FE RAILROAD SHOPS, CALIFORNIA)

A number of batch foam fractionation runs were made using Barstow waste water effluent. This effluent originated in the Sante Fe Railroad Shops in California and it contains more ABS (11.5 ppm) than do other secondary effluents from typical waste water treatement plants. The foam fractionation runs were made using a two inch diameter column, 30 inches long and a fine gas disperser. The air flow rate was varied from 17×10^{-3} to 63×10^{-3} SCF/min. and the residence time from 3 to 5 minutes.

The data indicate that increasing air flow rate from 17×10^{-3} to 63×10^{-3} SCF/min. decreases ABS concentration in the foamed liquid from 2.98 to 1.63 ppm and COD from 88 to 74 ppm. However, the foam overhead volume increases from 3.3 to 18.8% as the air flow rate is increased and this is undesirable because of the increased cost of disposing and handling large volumes of foam. Also, the enrichment ratios for ABS and COD are highest at the low air flow rates (Table 1 and Figure 1). Therefore, these data suggest that effluents high in ABS should be foamed using low air flow rates and possibly longer residence times. These Barstow effluent results should be compared and contrasted with those obtained with Bergen County, Middlesex County, and Bernardsville effluents described in the body of this report. The four different effluents studied are a useful indication of the variation of waste water effluent composition and foaming characteristics which may occur in practice.

Table 1

FOAM FRACTIONATION OF BARSTOW EFFLUENT

Run No.	pH	Residence Time, Min.	Air Flow Rate, SCF/Min.	Foam Overhead, Vol.%	ppm					% Removal		Enrichment Ratios C_F/C_L	
					COD	ABS	Cl	T.S.	V.S.	COD	ABS	COD	ABS
Feed	6.6	-	-	-	302	11.5	105	1088	180	-	-	-	-
184	7.7	5	17×10^{-3}	3.3	88	2.98	100	964	100	71	74	74	87
185	7.6	5	41×10^{-3}	14.5	102	2.93	100	966	94	66	74	14	21
187	7.7	5	63×10^{-3}	18.8	74	1.63	100	977	92	75	86	17	33
186	7.6	3	63×10^{-3}	7.9	168	2.98	100	937	108	44	74	11	37

Experimental Conditions:

200 cc. Barstow Effluent (unfiltered)
" Diameter Column, Fine Gas Disperser,
5°F., Batch Operation
oam Collected About 4.5" above Liquid Level in Column.

Figure 1a

FOAM FRACTIONATION OF BARSTOW EFFLUENT

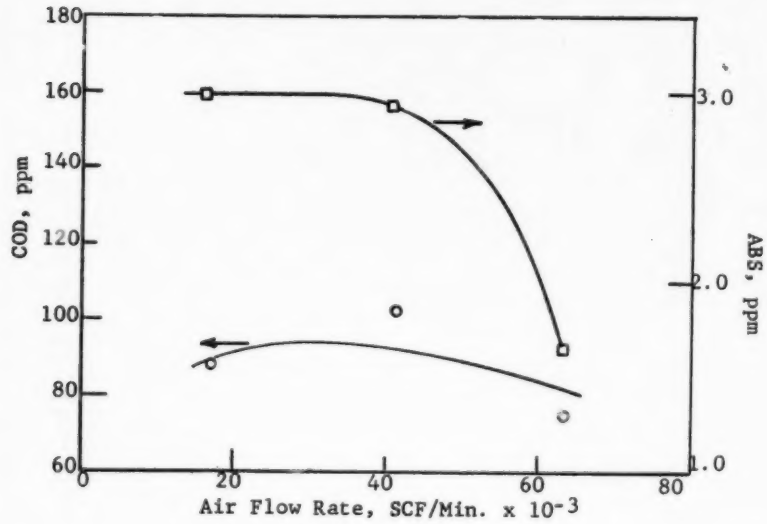


Figure 1b

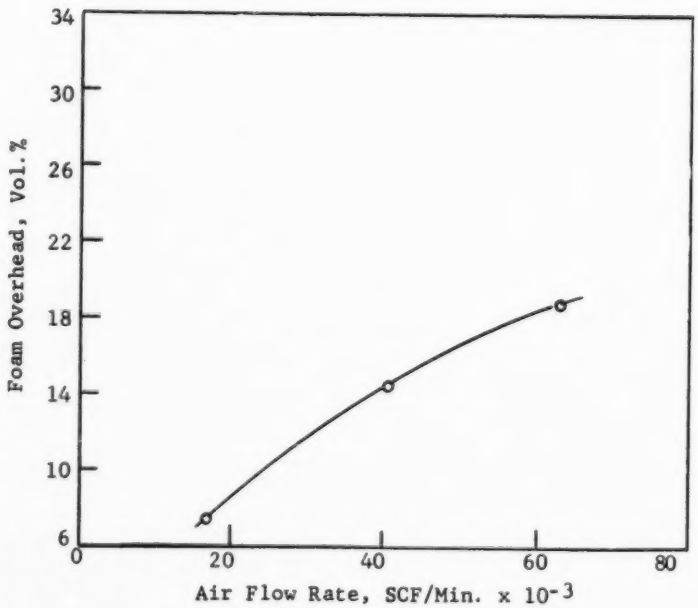
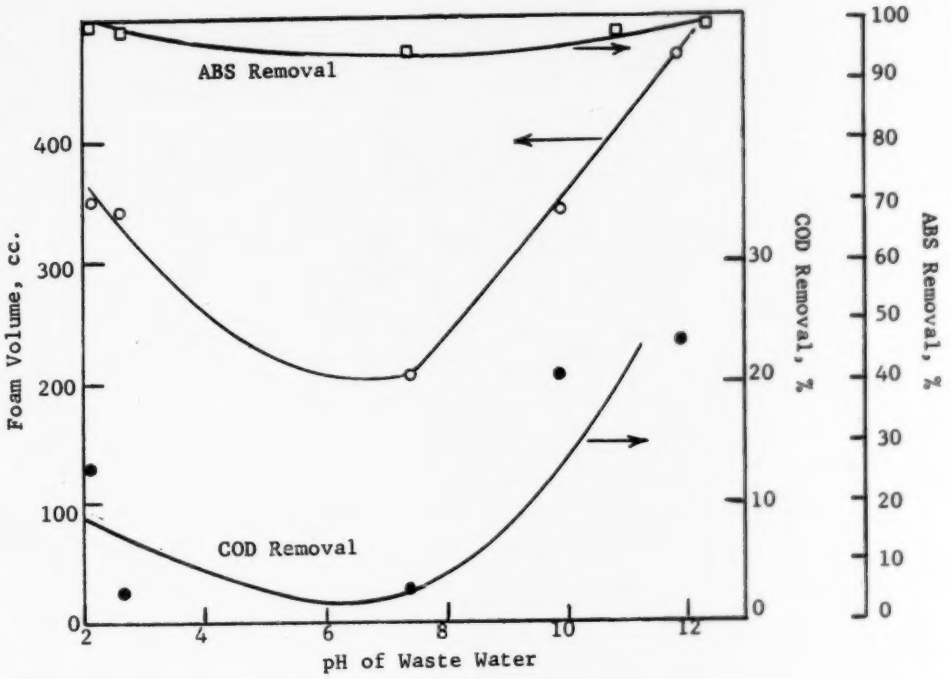


Figure 1c


ABS Removal
COD Removal
Foam Volume, cc.
COD Removal, %
ABS Removal, %
pH of Waste Water
0
100
200
300
400
10
20
30
40
50
60
70
80
90
2
4
6
8
10
12

APPENDIX G
REFERENCES

(1) F. Daniels, et al., "Experimental Physical Chemistry", McGraw-Hill Book Co., 1949.

(2) "Standard Methods for the Examination of Water and Waste Water", American Public Health Association, Inc., Edition 11, 1960.

(3) Eldib, I. A., "Foam Fractionation for Removal of Soluble Organics from Waste Water", Jour. Water Polln. Con. Fed., 914-931 (Sept., 1961).

(4) Gaden, E. L., and Schnepf, R. W., "Foam Fractionation of Proteins: Concentrations of Aqueous Solutions of Bovine Serum Albumin". Jour. Biochem. Microbiol. Tech. Eng., 1 (Feb., 1959).

(5) Lemlich, R., Elias, Lavi, "Foam Fractionation With Reflux", Science, 134, p. 191 (1961).

(6) Rogers, L. B., and Oliver, J. W., "Evaluating Reflux and Drainage in Foam Fractionations". Private Communication.

(7) Karger, B. L., and Rogers, L. B., Anal. Chem., 33, 1165 (1961).

(8) Walas, S. M., "Reaction Kinetics for Chemical Engineers".